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OPTIMAL PULSED PUMPING FOR AQUIFER REMEDIATION WHEN CONTAMINANT TRANSPORT IS AFFECTED BY RATE-LIMITED SORPTION: A CALCULUS OF VARIATION APPROACH

THESIS

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OPTIMAL PULSED PUMPING FOR AQUIFER REMEDIATION WHEN CONTAMINANT TRANSPORT IS AFFECTED BY RATE-LIMITED SORPTION: A CALCULUS OF VARIATION APPROACH

THESIS

Presented to the Faculty of the Graduate School of Engineering

of the Air Force Institute of Technology

Air Education and Training Command

In Partial Fulfillment

of the Requirements for the Degree of

Master of Science in Engineering and Environmental Management

Richard T. Hartman, B.S.

Captain, USAF

September 1994

Approved for public release; distribution unlimited

Acknowledgments

I am extremely grateful to those who believed and supported me in this effort and who allowed me to pursue this degree as a part-time student without too much pain. Hopefully this research effort will contribute and set the precedence for a pragmatic approach to groundwater remediation which is the foundation for a safe and healthy environment.

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Richard Thomas Hartman

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a	Immobile region radius or half width [L]
a_l	Longitudinal dispersivity [L]
b	Aquifer thickness [L]
$C'_m(r,t)$	Solute concentration in the mobile region [M/L^3]
$C_m(X,T)$	Dimensionless mobile region solute concentration
$\overline{C}_m(X,s)$	Dimensionless Laplace transformed volume-averaged mobile region solute concentration
$C'_{im}(r,t)$	Volume-averaged immobile region solute concentration [M/L^3]
$C_{im}(X,T)$	Dimensionless volume-averaged immobile region solute concentration
$\overline{C}_{im}(X,s)$	Dimensionless Laplace transformed volume-averaged immobile region solute concentration
D	Hydrodynamic dispersion coefficient [L^2/T]
$D_m(r)$	Mobile region dispersion coefficient [L^2/T]
D^*	Molecular diffusion coefficient [L/T]
K_d	Mobile region distribution coefficient [L^3/T]
Q(t)	Extraction well pumping rate [L^3/T]
r	Radial coordinate [L]
R_m	Mobile region retardation factor [unitless]
R_{im}	Immobile region retardation factor [unitless]
s	Laplace transform variable
S(r,t)	Sorbed contaminant [unitless]
t	Time variable [T]
T	Dimensionless time variable

$V(r)$	Seepage velocity [L/T]
$\lvert V(r) \rvert$	Magnitude of the seepage velocity [L/T]
$V_m(r)$	Mobile region seepage velocity [L/T]
X	Dimensionless radial distance variable
X_w	Dimensionless extraction well radius
X_∞	Dimensionless extraction well radius at infinity
α'	First-order rate constant [1/T]
α	Dimensionless first-order rate constant
β	Solute capacity ratio of immobile to mobile regions
θ	Aquifer porosity [unitless]
θ_m	Mobile region porosity [unitless]
θ_{im}	Immobile region porosity [unitless]
ρ	Bulk density of aquifer material [M/L^3]

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Abstract

The remediation of groundwater contamination continues to persist as a social and economic problem due to increased governmental regulations and public health concerns. Additionally, the geochemistry of the aquifer and the contaminant transport within the aquifer complicates the remediation process to restore contaminated aquifers to conditions compatible with health-based standards. Currently, the preferred method for aquifer cleanup (pump-and-treat) has several limitations including, the persistence of sorbed chemicals on soil matrix and the long term operation and maintenance expense. The impetus of this research was to demonstrate that a calculus of variations approach could be applied to a pulsed pumping aquifer remediation problem where contaminant transport was affected by rate-limited sorption and generalized to answer several management objectives. The calculus of variation approach produced criteria for when the extraction pump is turned on and off. Additionally, the analytic solutions presented in this research may be useful in verifying numerical codes developed to solve optimal pulsed pumping aquifer remediation problems under conditions of rate-limited sorption.

OPTIMAL PULSED PUMPING FOR AQUIFER REMEDIATION WHEN CONTAMINANT TRANSPORT IS AFFECTED BY RATE-LIMITED SORPTION: A CALCULUS OF VARIATIONS APPROACH

1. Introduction

General Issue

Groundwater accounts for 0.6 percent of the world's water and is the source of drinking water for 53 percent of the nation's population (Masters, 1991:104; Claborn & Rainwater, 1991:1290). Within the last several years, the quality of groundwater has become a sensitive issue both locally and nationally due to the years of accidental and/or deliberate disposal of hazardous materials into the ground soil. Historically, groundwater was considered a safe source of drinking water, however, groundwater sources are still contaminated by leachates from dumps, landfills, agriculture, septic tanks, cesspools, underground storage tanks, and chemical spills which continue to introduce various inorganic and organic solutes into aquifer systems (Masters, 1991:147; Ortolano, 1984:399). To address these issues the federal government has promulgated several strict and comprehensive laws, such as the Resource Conservation and Recovery Act (RCRA), the Superfund Amendments and Reauthorization Act (SARA) of 1986, and the Safe Drinking Water Act amendments of 1986.

The magnitude of this problem is reflected in the Environmental Protection Agencies (EPA's) National Priorities List (NPL) which lists over 1,200 sites. It has been estimated that "more than 70 percent of the nearly 1,200 hazardous waste sites on the NPL are contaminated with chemicals at levels exceeding federal drinking-water standards" (National, 1991:117). To address these problems the Department of Defense has engaged in a massive program to remediate all sites that pose a threat to public health, welfare, or the environment (U.S. Air Force IRP Remedial Project Manger's Handbook, 1989:1-1). This program is known as the Installation Restoration Program (IRP).

One of the most ubiquitous groundwater contaminants are volatile organic compounds (VOCs). Today, interest in VOC contamination persists due to the prevalence of VOC groundwater contamination, the potential chronic health concerns associated with these organic chemicals, and the observed difficulties encountered with groundwater remediation at VOC contaminated sites (Haley et. al., 1991:120; MacKay & Cherry, 1989:630). One of the factors limiting the effective removal of these contaminants is the sorption of these contaminants to the aquifer media, that is, sorbed contaminant mass may be on the same order or greater than the dissolved contaminant mass (Haley et. al., 1991; MacKay & Cherry, 1989). This mass of sorbed contaminants is often not accounted for in aquifer restoration and confounds the ability to remediate contaminated aquifers to a condition compatible with health-based standards.

To help describe and predict the behavior of groundwater flow and solute transport, the nature of the aquifer contaminant system can be described by mathematical models (Mercer & Faust, 1981:1). Mathematical models are useful tools that help the hydrologist determine the fate and transport of contaminants. Today, many groundwater models exist which describe groundwater flow and solute transport. However, due to the complexity of the subsurface it is virtually impossible to model all of the mechanisms impacting contaminant fate and transport.

Traditionally, the advection-dispersion equation has been used to model contaminant transport. This equation uses a retardation factor to account for sorption. Use of a retardation factor implicitly assumes local equilibrium between contaminant in the sorbed and aqueous phases (Lapidus & Amundson, 1952:984). Largely due to mathematical simplicity, the local equilibrium assumption (LEA) is frequently used to simulate solute transport. Recently, however, experimental observations from the laboratory and the field have provided evidence that, at least in certain cases, the LEA is not valid (Goltz, 1991:24; Goltz & Roberts, 1988:61).

These problems are associated with two phenomena called *tailing* and *rebound*. *Tailing* is the asymptotic decrease in the contaminant concentration in extracted water after a relatively rapid initial decrease. *Rebound* is the increase in contaminant concentration after cessation of pumping (Adams & Viramontes, 1993:1-4). These phenomena are usually observed years after the pump-and-treat process has been ceased and the hazardous waste site is closed (Travis & Doty, 1990:1465; Mackay and Cherry, 1989:633). Fortunately, these phenomena can be described by rate-limited sorption/desorption, since it appears that the contaminant in the sorbed and aqueous phases do not equilibrate instantly but reach equilibrium slowly (Adams & Viramontes, 1993:1-4).

Unfortunately, groundwater models used today in aquifer cleanup efforts at Air Force IRP sites do not account for rate-limited sorption/desorption (Goltz & Oxley, 1990). This can lead to an underestimation of aquifer cleanup time and premature cessation of pumping to control contamination (Goltz & Oxley, 1991:554). Ultimately, this results in desorption and reintroduction of the contaminant into an aquifer that was presumed to be clean. Obviously, use of such models which do not incorporate rate-limited sorption/desorption may additionally create social and economic impacts by promoting a false sense of security to the community and an increase in treatment cost.

Social and legal impacts of remediation require that contaminated sites be cleaned up to health-based standards that are mandated by Federal, State, and Air Force regulations. "This remediation usually involves the treatment of water pumped from the ground." (Greenwald & Gorelick, 1989:73) In fact, the most widely used method of groundwater treatment involves pump-and-treat techniques for aquifer remediation, where contaminated groundwater is removed from the ground by wells, treated and disposed

(Ammons, 1988;1). Additionally, the EPA predicts that pump-and-treat methods will remain to be the remedy of choice at least in the foreseeable future (McKinney & Lin, 1992:695).

Groundwater remediation still remains one area where technology has failed to achieve health-based cleanup goals (Travis & Doty, 1990:1465). Since the characteristics of contaminant transport affected by rate-limited sorption imply slow removal (i.e., removal of the waste over a longer time period) and increased water treatment when compared with equilibrium sorption, one would predict an increase in remediation cost when transport is affected by rate-limited sorption. As of today, several models have been created describing optimal methods for groundwater plume removal under the LEA. In fact, only recently have groundwater models addressed the effects of rate-limited sorption (Adams & Viramontes, 1993; Huso, 1989; Harvey, Haggerty & Gorelick, 1993). Despite this fact, none have incorporated an optimal method for groundwater remediation affected by rate-limited sorption/desorption. If pumping rates can be optimized to create a pumping schedule with a more representative model of the contaminant transport, contaminated water may be removed more efficiently and cost effectively to health based cleanup goals.

Specific Problem

The purpose of this research is to use a calculus of variation approach to derive and test a set of management criteria described by objective functionals and constraints that account for the economic, social, physical and chemical concerns related to pulsed pumping aquifer remediation. More importantly, these functionals and constraints should model aquifer remediation when contaminant transport is affected by rate-limited sorption.

Research Objectives

The specific objectives of this research are:

1. Develop objective functionals which address cleanup cost, cleanup time, mass of contaminant removed, risk, etc. at a single extraction/monitoring well.

2. Modify an existing contaminant transport equation to allow for rate-limited sorption measured at a single extraction/monitoring well.

3. Form the finite time horizon optimization problem for the minimization of the objective functional over the set of pulsed pumping schedules subject to contaminant transport in a radially symmetric infinite aquifer.

4. Develop necessary and sufficient optimality conditions for pulsed pumping schedules for the finite time horizon optimization problem.

5. Determine the optimal pulsed pumping schedules for various objective functionals using the simple case of contaminant transport in a radially symmetric infinite aquifer affected by rate-limited sorption.

Scope and Limitations of the Research

This research details the development of a general optimization problem which incorporates an objective functional and constraints and will use Lagrange multiplier theory. A calculus of variation approach will be taken to solve the problem. Since this research is predominantly a proof of concept, the scope of the research will concentrate on the transport of a contaminant for an ideal model aquifer. The prevailing limitations of this research are the physical and chemical constraints of the transport equation (i.e., the final results are only as good as the transport equation and the assumptions in the formulation of the transport equation).

The transport equation for this research will describe the physical and chemical behavior of groundwater flow and contaminant transport from an extraction well for a radially symmetric aquifer that is infinite in aerial extent including: advection, dispersion, and rate-limited sorption/desorption. The equation will not address confounding problems usually present in an aquifer system, such as precipitation or the effects of drawdown, since it is assumed that an infinite amount of water is stored in the aquifer. The material within the aquifer will be homogenous and isotropic, the concentration will be limited (i.e., no external sources of pollution) and molecular diffusion in the mobile region will be much smaller than the dispersion due to the flow rate caused by the pump near the well.

Lastly, necessary and sufficient optimality conditions will be thoroughly evaluated for the general problem using a calculus of variation approach through the evaluation of the dependent variables of the integral incorporating both the objective functional and the constraints.

Definitions

Key terms associated with contaminant transport and aquifer remediation are listed below. Unless otherwise noted they are Environmental Protection Agency (EPA) definitions (EPA, 600/8-90/003, 1990; EPA, 540/S-92/016, 1993).

1. Absorption: A uniform penetration of the solid by a contaminant.
2. Adsorption: An excess contaminant concentration at the surface of a solid.
3. Advection: The process whereby solutes are transported by the bulk mass of flowing fluid.
4. Aquifer: A geologic unit that contains sufficient saturated permeable material to transmit significant quantities of water.

5. Breakthrough Curve: Contaminant concentration versus time relation (Freeze & Cherry, 1979:391).
6. Cleanup: The attainment of a specified contaminant concentration (Goltz & Oxley, 1991:547).
7. Concentration Gradient: Movement of a contaminant from a region of high concentration to a region of lower concentration (Freeze & Cherry, 1979:25).
8. Desorption: The reverse of sorption.
9. Diffusion: Mass transfer as a result of random motion of molecules. It is described by Fick's first and second law.
10. Dispersion: The spreading and mixing due to microscopic variations in velocities within and between pores.
11. Homogeneous: A geologic unit in which the hydrologic properties are identical from point to point.
12. Pulsed Pumping: A pump-and-treat enhancement where extraction wells are periodically not pumped to allow concentration in the extracted water to increase.
13. Retardation: The movement of a solute through a geologic medium at a velocity less than that of the flowing groundwater due to sorption or other removal of the solute.
14. Sorption: The generic term used to encompass the phenomena of adsorption and absorption.
15. Tailing: The slow, nearly asymptotic decrease in contaminant concentration in water flushed through contaminated geologic material.

Overview

This thesis consists of five chapters. Chapter 1 identified that remediation models which do not account for the phenomena of rate-limited sorption can lead to an underestimation of cleanup time creating the potential reintroduction of contaminants into the aquifer (Goltz & Oxley, 199:547). Optimization was also suggested as a tool to be utilized with pump-and-treat remediation that will address the economic, social, physical and chemical concerns related to groundwater contamination. Chapter 1 concludes with a research proposal to develop and test a calculus of variation approach to determine optimal pulsed pumping for aquifer remediation when contaminant transport is affected by rate-limited sorption.

Chapter 2 consists of a thorough literature search highlighting groundwater optimization and contaminant transport modeling. It will review the problems associated with sorption and desorption, address the transport equation to be modified, and introduce the rationale behind the proposed pulsed pumping strategy. It will also discuss the historical evolution of groundwater remediation optimization techniques. Chapter 2 will conclude with a summary of the literature and end with the motivation for this particular research.

Chapter 3 will focus on the development of the general optimization problem and the specific optimization problem statement. It will address several issues including the necessary optimality conditions for the first and second variation and the sufficient optimality conditions to ensure that the physics and mathematics utilized correctly meet the objective to create a management tool which will determine an optimized pulsed pumping schedule for aquifer remediation when contaminant transport is affected by rate-limited sorption/desorption. A procedure will also be described to determine an optimal solution to the mathematics described dependent on the management objective.

Chapter 4 will apply the findings from Chapter 3 and identify eight subclasses of objective functionals. From these eight subclasses, general cases will be developed and evaluated analytically to determine interesting/non-interesting and trivial/nontrivial cases from a management perspective for groundwater remediation when contaminant transport is affected by rate-limited sorption. Specific examples will be evaluated and the analytical solutions will provide management decisions for either a pulsed pumping strategy, a continuous pumping strategy, or not to pump at all for specific objective functionals. Chapter 5 will summarize the research and develop conclusions from the findings and recommend follow-on research.

2. Literature Review

Introduction

Groundwater remediation remains one area where technology has failed to produce clear solutions to health-based cleanup goals (Travis & Doty, 1990:1465). As limitations of pump-and-treat become more apparent, the search continues for new ways to treat subsurface contamination (Harris, 1991:48).

It has been found through field studies and mathematical modeling that rate-limited sorption/desorption can have a profound effect on the transport of sorbing organic contaminants (Goltz & Roberts, 1988; Nkedi-Kizza, P., Rao, Jessup, & Davidson, 1982; VanGenuchten & Wierenga, 1976). Currently, the models used to help plan aquifer cleanup efforts at Air Force Installation Restoration Program (IRP) sites do not account for rate-limited sorption/desorption (Goltz & Oxley, 1990). Rate-limited sorption is due to the slow diffusion of solute through zones of unsaturated or slow flow. The theoretical work done by Goltz and Oxley (1991) demonstrates that overlooking rate-limited sorption effects can lead to an underestimation of aquifer cleanup time (Goltz & Oxley, 1990).

Due to the tailing effect observed in aquifers affected by rate-limited sorption, pump-and-treat remediation has been criticized. This criticism evolves from the fact that large volumes of water are treated only to remove minimal amounts of contaminant at a high cost and not necessarily to health-based standards (Goltz & Oxley, 1991:547; Mackay and Cherry, 1989:630; Keely and others, 1987:94; Olsen and Kavanaough, 1993:44). An alternative method to resolve this problem is a pulsed pumping schedule which allows desorption to occur during periods when the pumps are turned off (Keely and others, 1987:94).

Additionally, to address the high operational cost of aquifer remedial designs optimization models have been developed to minimize the cost of aquifer remediation. The goal of the optimization approach is to evaluate and increase the efficiency and cost effectiveness of current remediation techniques (McKinney & Lin, 1992:695). In particular, pump-and-treat methods have been addressed since they are the preferred method of remediation and continue to be associated with high operational cost. Optimization to date has mainly concentrated on remediation techniques which determine static (steady state) methods in which pumping does not change over time (Culver & Shoemaker, 1993:823).

This literature review will describe past and current research efforts to remediate groundwater contamination using pump-and-treat methods while also addressing optimal pumping strategies for both contaminant cleanup and containment. The literature review is divided into four sections: (1) aquifer model development, (2) optimal pumping strategies without the use of formal optimization techniques (e.g., pulsed pumping), and (3) optimization of remediation models involving extraction and/or treatment with the use of formal optimization techniques. This chapter concludes with a discussion on the relation between the problems discussed in the literature and the problem addressed in this thesis.

Aquifer Model Development

This section of the literature review will discuss the evolution of mathematical models used to simulate the transport of contaminants. This will range from the advective/dispersion model with linear sorption to the transport of contaminant affected by rate-limited sorption/desorption in the immobile regions of the aquifer.

There are several ways to pose the physical and chemical nature of the contaminant transport. Traditionally, the advection-dispersion equation has been used to model contaminant transport. The classical dispersion model in cylindrical coordinates (Valocchi, 1986:1693), is given by:

$$\frac{\partial C'(r,t)}{\partial t}+\frac{\rho}{\theta}\frac{\partial S(r,t)}{\partial t}=\frac{1}{r}\frac{\partial}{\partial r}\left[rD'\frac{\partial C'(r,t)}{\partial r}\right]-V'(r)\frac{\partial C'(r,t)}{\partial r} \tag{2.1}$$

where the symbols are defined by

$C'_m(r,t)$	contaminant concentration in the mobile zone [M/L^3]
r	radial coordinate [L]
t	time [T]
S(r,t)	sorbed contaminant [unitless]
V'(r)	seepage velocity [L/T]
ρ	bulk density of aquifer material [M/L^3]
θ	aquifer porosity [unitless]

The term D' is the hydrodynamic dispersion coefficient [L^2/T] and is described by

$$D' = a_l|V(r)| + D^* \tag{2.2}$$

where a_l is the longitudinal dispersivity of the porous medium [L], $|V'(r)|$ is the magnitude of the seepage velocity [L/T], and D^* is the molecular diffusion coefficient [L/T]. The seepage velocity for the steady state cylindrical aquifer is given by:

$$V'(r)=\frac{-Q(t)}{2\pi b\theta r} \tag{2.3}$$

where Q(t) is the constant pumping rate at the well [L^3/T], and b is the aquifer thickness [L].

When the pump is turned on, the molecular diffusion D^* is negligible close to the well when compared to the mechanical dispersion $a_l|V'(r)|$ (Valocchi, 1986:1694). However, when the pump is turned off, it is believed that the opposite occurs and that molecular diffusion is dominant in comparison with the mechanical dispersion.

Models generally differ in the characterization of the $\frac{\partial S}{\partial t}$ term (Weber and others, 1991:505). The simplest model to describe the accumulation of solute by the sorbent is usually represented by $S = K_d C$, where K_d is the partition coefficient [L^3/M] reflecting the sorption, which implies that the accumulation of the solute by the sorbent is directly proportional to the solution phase concentration (Domenico & Schwartz, 1990:441). Substituting this equation into equation (2.1) creates:

$$R\frac{\partial C'(r,t)}{\partial t}+\frac{\rho}{\theta}\frac{\partial S(r,t)}{\partial t}=\frac{1}{r}\frac{\partial}{\partial r}\left[rD'\frac{\partial C'(r,t)}{\partial t}\right]-V'(r)\frac{\partial C'(r,t)}{\partial r} \tag{2.4}$$

This equation uses a retardation factor, $R = 1+\frac{\rho K_d}{\theta}$ [unitless] to account for sorption that assumes local equilibrium assumption (LEA) between contaminant in the sorbed and aqueous phases. Recently, however, it has been identified in other investigations,

> that experimentally obtained breakthrough responses exhibited sharper initial breakthrough and more tailing than would be predicted using models that assume linear, reversible, equilibrium sorption. (Goltz and Roberts, 1986, p. 81)

Due to the assumption of equilibrium sorption, the affects of rate-limited sorption/desorption were not considered. This creates a problem because the time to clean a contamination site is underestimated. To address this problem Goltz and Oxley developed a mathematical model describing the transport of a single sorbing solute in a radially flowing aquifer in a porous medium with immobile water regions:

$$\frac{\partial C'_m(r,t)}{\partial t} = \frac{D'_m(r)}{R_m}\frac{\partial^2 C'_m(r,t)}{\partial r^2} - \frac{V'_m(r)}{R_m}\frac{\partial C'_m(r,t)}{\partial r} - \frac{\theta_{im} R_{im}}{\theta_m R_m}\frac{\partial C'_{im}(r,t)}{\partial t} \tag{2.5}$$

where the symbols are defined by:

$C'_m(r,t)$	solute concentration in the mobile region $[M/L^3]$
$C'_{im}(r,t)$	volume-averaged immobile region solute concentration $[M/L^3]$
$V'_m(r)$	mobile region seepage velocity [L/T]
$D'_m(r)$	mobile region dispersion coefficient $[L^2/T]$
θ_m	mobile region porosity [unitless]
θ_{im}	immobile region porosity [unitless]
R_m	mobile region retardation factor [unitless]
R_{im}	immobile region retardation factor [unitless]

where

$$V'_m(r) = \frac{-Q(t)}{2\pi b\theta r} \tag{2.6}$$

and

$$D'_m = a_1|V(r)| + D^* \tag{2.7}$$

This expression assumes that sorption onto the solids is linear and reversible, with the effect of sorption incorporated into R_m and R_{im}, where $R_m = 1 + \frac{\rho f K_d}{\theta_m}$,

$R_{im} = 1 + \frac{\rho(1-f)K_d}{\theta_{im}}$, and f is the fraction of sorption sites adjacent to regions of mobile water (Adams & Viramontes, 1993:2-14). This model also assumes that solute transfer between the mobile and immobile regions can be described by a first-order differential equation:

$$\frac{\partial C'_{im}(r,t)}{\partial t} = \frac{\alpha'}{\theta_{im} R_{im}} \left[C'_m(r,t) - C'_{im}(r,t) \right] \tag{2.8}$$

where α' is a first-order rate constant [1/T] and it is assumed that the solute transfer is a function of the solute concentration difference between the mobile and immobile regions. This combination of equations describes the two-region first-order sorbing solute transport (Adams & Viramontes, 1993). Since this mathematical model describes the phenomena of rate-limited sorption it is the most appropriate transport constraint for the optimization problem.

Note that if both the Valocchi equation (2.1) and the Goltz & Oxley equation (2.5) are combined the equation which incorporates both molecular diffusion and mechanical dispersion follows:

$$\frac{\partial C'_m(r,t)}{\partial t} = \frac{1}{R_m}\frac{1}{r}\left(\frac{a_l Q'(t)}{2\pi b \theta_m} + rD^*\right)\frac{\partial^2 C'_m(r,t)}{\partial r^2} + \frac{1}{R_m}\frac{1}{r}\left(\frac{Q'(t)}{2\pi b \theta_m} + D^*\right)\frac{\partial C'_m(r,t)}{\partial r} - \frac{\theta_{im} R_{im}}{\theta_m R_m}\frac{\partial C'_{im}(r,t)}{\partial t} \tag{2.9}$$

Using equations (2.8) and (2.9), the effects of rate-limited sorption can be addressed as the transport constraint for the optimization problem.

The next two sections will discuss the proposed optimal pumping strategy (pulsed pumping) to be utilized with the transport equations along with remedial optimization techniques.

Optimal Pumping Strategies

The most prevalent method of remediation is pump-and-treat. This well water pumping technique has existed for a reasonable time, but has not seriously addressed the various problems associated with the cost and ability to reach health-based standards. In fact, this approach has been severely criticized primarily due to its ineffectiveness in achieving health-based cleanup standards coupled with extended periods of cleanup and high cost. Additionally, these methods have not addressed aquifers where rate-limited sorption/desorption is significant. This section will address an alternative pumping schedule that can account for rate-limited sorption/desorption and potentially provide an optimal pumping strategy.

Due to the persistence of residual contamination where pumping may be continued indefinitely or may lead to premature cessation of the remediation and closure of the site, Keely et al. (1987) recognized the problems of conventional groundwater contamination remediation which typically involve continuous operation of an extraction-injection wellfield. Their solution was an alternative pumping scheme that would optimize contaminant residual recovery by a pulsed pumping technique. This pulsed operation of the hydraulic system cycles extraction or injection wells on and off in 'active' and 'resting' phases, where the resting phase allows time for residual contaminants to migrate into the mobile region and the active cycle will remove the minimum volume of contaminated groundwater, at the maximum possible concentration, for the most efficient treatment (Keely et al., 1987:99).

Carlson (1989) created a numerical model based on the physical principle of mobile and immobile zones and tested it using a pulsed pumping strategy. This model verified that if the pumping is ceased before the immobile region is reduced significantly, the concentrations in the mobile region increase with time.

Borden and Kao (1992) performed column experiments to test and examine the kinetics of aromatic hydrocarbon dissolution as residual hydrocarbon ages. They also developed a mathematical model to aid in the analysis of the experimental data and simulate the efficiency of groundwater extraction systems for remediation of contaminated aquifers in which non-aqueous-phase hydrocarbon is present as immobile globules. This numerical model was used to evaluate three different remediation alternatives for a hypothetical aquifer. These alternatives where: (1) constant pumping rate, (2) reduced pumping rate and (3) pulsed pumping. It was noted that of the three remediation alternatives, pulsed pumping may result in a greater amount of hydrocarbon recovered per volume of water, but may increase the time to meet a required standard, since the long-term efficiency of soil-flushing systems seems to be limited by the rate of aromatic hydrocarbon transfer between larger oil globules and the aqueous phase (Borden & Kao, 1992:35).

Adams & Viramontes (1993) extended Carlson and others work by developing a source code based on their solutions to the transport equation. They presented equations governing contaminant transport affected by rate-limited sorption during aquifer remediation by pulsed pumping. They analytically solved the transport equation in the Laplace domain using a Green's function technique and then performed a Laplace inverse transform numerically to invert it back into the time domain. Their simulations indicate that pulsed pumping operations can improve the efficiency of pump-and-treat remediation of aquifer contamination.

Harvey et al. (1993), investigated pulsed pumping techniques and observed problems with rebound due to the mass transfer from the immobile region to the mobile region when the pump is turned off. They compared pulsed pumping to continuous pumping (i.e., continually pumping at a constant rate) for a contaminant plume subject to first order mass transfer during transport in an aquifer with no natural gradient. They created several scenarios and determined contrary to the previous citations, that pulsed pumping does not remove more mass of contaminant than an equivalent continuous pumping rate where the same amount liquid volume was removed. Additionally, they stated that for low continuous pumping rates and short pulsed pumping periods, pulsed pumping is less efficient than continuous pumping. However, due to reduced pumping time, savings in labor cost or the shared cost of treatment systems, pulsed pumping may be preferable to continuous pumping.

This section discussed methods to optimize the remediation of contaminant sites through the use of pumping techniques which did not utilize any formal optimization method other than trial and error simulation. The next section will investigate methods which truly attempt to combine remediation with optimization theory.

Remediation Models Utilizing Optimization Techniques

Remediation projects designed around pump-and-treat methods are typically accomplished with trial-and-error simulation of feasible combinations of pump locations and pumping rates. Given the countless numbers of feasible remediation designs for a given problem, an optimal management solution may never be identified by trial-and-error simulation. To address this problem mathematical optimization techniques combined with transport simulation can efficiently search through the potential design options and thus be a useful tool for planning cost effective pump-and-treat groundwater remediation (Culver & Shoemaker, 1992:629). This section of the literature review will address the evolution of optimization techniques to provide cost effective strategies for groundwater remediation.

In the early 1980's Gorelick published a comprehensive review of numerical models which solve groundwater flow or solute transport equations in conjunction with optimization techniques as aquifer management tools. Up to this time numerical models primarily aided in the evaluation of groundwater resources. These same models were then coupled with optimization methods to manage hydraulic gradients for groundwater wells.

As the threat to groundwater supplies became more evident, the necessity to cleanup these contaminated sites increased due to potential health concerns and the promulgation of several stringent federal requirements. Unfortunately, groundwater remediation was only in its infancy and the most convenient method to prevent contaminant plume migration from affecting regional groundwater supplies was to contain the contaminant while effective cleanup strategies were being developed. Several studies addressed this strategy while attempting to make it efficient. Eventually the scientific community addressed the containment of a contaminated groundwater plume by minimizing the pumping as a management tool (Gorelick, 1983; Gorelick & Atwood, 1985; Ahlfeld & others, 1986). "These initial methods for plume management included constraints on heads, gradients, and velocities but did not account for concentration or cleanup time in any way." (Greenwald & Gorelick, 1989: 75) For example, Gorelick and Atwood (1985) demonstrated an optimal containment strategy combining a solute transport model with a management technique of linear programming referred to as the simulation-management model that would minimize the amount of water to be extracted during extraction and injection. However, these containment methods only stabilized the hydraulic gradient and did not really address the real problem of contamination cleanup.

It was not long until Lefkoff and Gorelick (1985) recognized real remediation problems faced by both government and industry and utilized groundwater flow simulation and mathematical optimization as a groundwater remediation tool. Their optimization remediation goal was to remove a contaminant plume from a hypothetical aquifer in four years, since design criteria for a restoration project may require a target date for contaminant removal. An optimal pumping and injection schedule was created that used a response matrix method, which requires the physical system (e.g., heads, gradients and velocities) to respond linearly to changes in the pumping or injection (i.e., utilizes the principle of linear superposition). They assumed purely advective flow and did not account for hydrodynamic dispersion. The objective function to be minimized modeled the cost per unit volume pumped and the pumping rate. The study demonstrated the utility of simulation-optimization models, however, it also identified the difficulty and expense of rapid restoration, because large volumes of water must be pumped and treated.

Ahlfeld et al. (1988) proposed two nonlinear optimization formulations designed to find a pumping system which removes the most contaminant during a fixed time period and reduces the contaminant concentration to regulated levels at the end of the fixed time at minimum cost. Their optimization formulations combined advective-dispersive contaminant transport simulation with nonlinear optimization. To address the concerns of the decision maker they presented two alternative optimization formulations; one to minimize residual contaminant in the aquifer and the other to minimize the cost. The objective functions described were discrete and dependent on several constraints concerned with either: (1) the objective to remove the contaminant at a given time or (2) to meet regulatory requirements at a minimum cost. The results of their proposed methods were reinforced by field studies which indicated that their formulations modeled the technical aspects of remediation design based on different management perspectives, again, to either "(1) remove as much contaminant as possible with given constraints on the total pumping or (2) satisfy quality standards at minimum cost with no regard for the fate of the groundwater contaminant at unmonitored locations". (Ahlfeld & others, 1988: 451)

Greenwald and Gorelick (1989) again recognized the problems associated with the cost of long-term remediation of groundwater contamination and developed a cleanup strategy that would minimize the time it takes to removal all contaminants from the aquifer. They used a quasi-analytic solution for advective contaminant transport in combination with nonlinear optimization which uses an objective function involving pumping rates, injection rates and cleanup time, where cleanup time was either fixed or ignored. Using an advective transport model and treating cleanup time as a continuous management variable, they show that the cleanup time will be affected by pumping rates. Unfortunately, the ability to address complex hydrological systems is limited to the simulation model which only incorporates advection.

Kuo et al. (1991) introduced a simulated annealing algorithm to address problems present with current optimization techniques due to constraint equations and nonsmooth cost functions. Two nonlinear optimization formulations of interest were proposed: (1) to reduce plume concentration to a specified regulation standard within a specified time while minimizing cost under hydrodynamic constraints, and (2) to minimize residual contaminant in a fixed period under hydraulic constraints only. Again discrete objective functions were used to form the optimization problem with a simulation model that addressed both advection and dispersion. Different pumping strategies were generated for different problem formulations. Of interest is that bang-bang controls (i.e., pump-on, pump-off, etc.) were used to determine optimal pump-and-treat strategies for groundwater remediation, using the simulated annealing algorithm.

Methods to optimize the remediation of contaminated sites through the use of various optimization techniques were addressed. However, the typical transport equation used has been with a simplified advection model or an advection-dispersion equation using local equilibrium assumptions without addressing the effect of rate-limited sorption/desorption. Additionally, objective functionals utilized for the various optimization techniques were in a discrete form in order to perform numerical analysis as opposed to an integral form to perform analytical analysis.

Conclusion

Of all the existing environmental problems, water quality issues remain to prove difficult and expensive to solve where groundwater contamination is still recognized as the most difficult and important issue to solve (Helsing, 1988:35). The most prevalent technique used by the U.S. Air Force for contaminant remediation affecting groundwater sources in the saturated zones involves pump-and-treat. However, this remediation method has limitations meeting health-based water quality standards, particularly when contamination involves the sorption of petroleum hydrocarbon constituents. Due to the tailing affect observed in aquifers affected by rate-limited sorption, pump-and-treat remediation has been criticized. Again, this criticism revolves around the fact that large volumes of water are treated only to remove a minimal amount of contaminant not necessarily to health-based standards.

An alternative method, pulsed pumping, was presented to resolve this problem by allowing desorption to occur during periods when or while the pumps are turned off. Current literature is not definitive on the affects of pulsed pumping. Additionally, no one to date has developed a pulsed pumping schedule that utilizes mathematical optimization techniques employing rate-limited sorption.

Several optimization methods were also addressed which described work related to cost effective remediation techniques, but have not determined a proper method for contamination cleanup due to the inappropriateness of the advection-dispersion equation for aquifers where sorption is significant. Additionally, an analytical approach has not been developed and only numerical methods or quasi-analytical methods specifically related to the transport equation have been identified.

The goal of the this thesis is to modify an existing groundwater transport model (Adams & Viramontes, 1993) that incorporates rate-limited sorption and couple it with an optimization technique using a calculus of variation approach. This will be accomplished by combining the existing sorption/desorption transport theory with an objective functional and utilizing a calculus of variations approach. With this general approach, objective functionals can be varied to accommodate the various management decisions for groundwater remediation.

This research will provide information and insight into the management of pump-and-treat cleanup operations at U.S. Air Force Installation Restoration Program sites and how to best remediate contaminated sites where rate-limited sorption/desorption is prevalent. More importantly, this research focuses on the development of a pragmatic groundwater contamination cleanup approach to health-based standards while addressing the excessive cost of remediation.

3. Analysis and Methodology

Introduction

Field studies and mathematical modeling have revealed that rate-limited sorption/desorption can greatly affect the transport of sorbing organic contaminants (Goltz & Roberts, 1988; Nkedi-Kizza, P., Rao, Jessup, & Davidson, 1982; VanGenuchten & Wierenga, 1976). Currently, groundwater models used in aquifer cleanup efforts at U.S. Air Force Installation Restoration Program (IRP) sites do not account for rate-limited sorption/desorption (Goltz & Oxley, 1990). This can lead to an underestimation of aquifer cleanup time and premature cessation of pumping to control contamination (Goltz and Oxley, 1991).

The preferred method for aquifer cleanup (pump-and-treat) has several limitations including, the persistence of sorbed chemical on soil matrix and the long term operation and maintenance expense. These problems motivate the necessity to optimize this existing remediation technology while accounting for rate-limited sorption. Unfortunately, optimization techniques developed to date have not considered the effects of rate-limited sorption/desorption.

The objective of this thesis is to create a management tool where a set of objective functionals can be optimally evaluated for economic, social, physical and chemical constraints related to pulsed pumping aquifer remediation when contaminant transport is affected by rate-limited sorption in a finite time. In order to determine an optimal pumping schedule, a calculus of variation approach is utilized as the preferred optimization technique where the contaminant transport equation from Adams and Viramontes (1993) is modified to examine contaminant concentrations measured at the extraction well.

This chapter will discuss the basic premise of optimization and the calculus of variations, along with the model assumptions and aquifer characteristics. A generalized form of the objective functional will be described, the transport equation will be written, and the optimization problem will be formed. Lastly, the necessary and sufficient optimality conditions will be given which will motivate the solution to the partial differential equations describing pulsed pumping .

Optimization and Calculus of Variations

Optimization techniques originally were developed from the field of Operations Research (Walbridge, 1985:4). They generally identify optimization problems which either *maximize* or *minimize* the value of a particular objective functional while satisfying certain constraints or restrictions. The objective functional and the constraints are generally expressed as functions of a set of decision variables (Walbridge, 1985:4). As noted in Chapter 2, optimization techniques have expanded and been applied to groundwater remediation problems providing an additional tool to provide an efficient means to cleanup contaminated groundwater in a timely manner. However, in this thesis a calculus of variations approach will be considered.

In general, calculus of variations is an area of mathematics which involves problems where the quantity to be minimized or maximized appears in the form of an integral. In ordinary calculus candidates for the minimum and maximum values are found by taking the derivative of the function, say F(x), setting it equal to zero and solving for a root(s). If the values of $\hat{x}$ correspond to relative maximum values, minimum values or points of inflection with a horizontal tangent then $\hat{x}$ satisfies the equation $F'(\hat{x}) = 0$ (Boas, 1983:383). The equation $F'(\hat{x}) = 0$ is a necessary (but not sufficient) condition for all the values of $\hat{x}$ that may be maxima, minima or saddle points (Arfken, 1985:926). Further mathematical tests and/or the physical description of the problem are required to determine whether or not a point $\hat{x}$ yields a maximum, minimum or point of inflection. These will be appropriately discussed starting with the model assumptions and aquifer characteristics.

Model Assumptions and Aquifer Characteristics

Since this work extends the work of Huso (1989), Goltz & Oxley (1991), and Adams & Viramontes (1993), the equations, solutions, notation, and assumptions will based on their papers.

Aquifer description. There are several assumptions in the formation of the model used to describe the contaminant transport analytically. Listed below are the simplifying assumptions used to represent an ideal scenario.

First, contaminant transport is described by steady, uniform, converging radial flow resulting from advection created by the extraction well. Therefore, both head drawdown due to pumping and contaminant transport due to a natural groundwater gradient are ignored (see Figure 3.1). Additionally, the head of the aquifer is constant when compared with the water movement due to pumping.

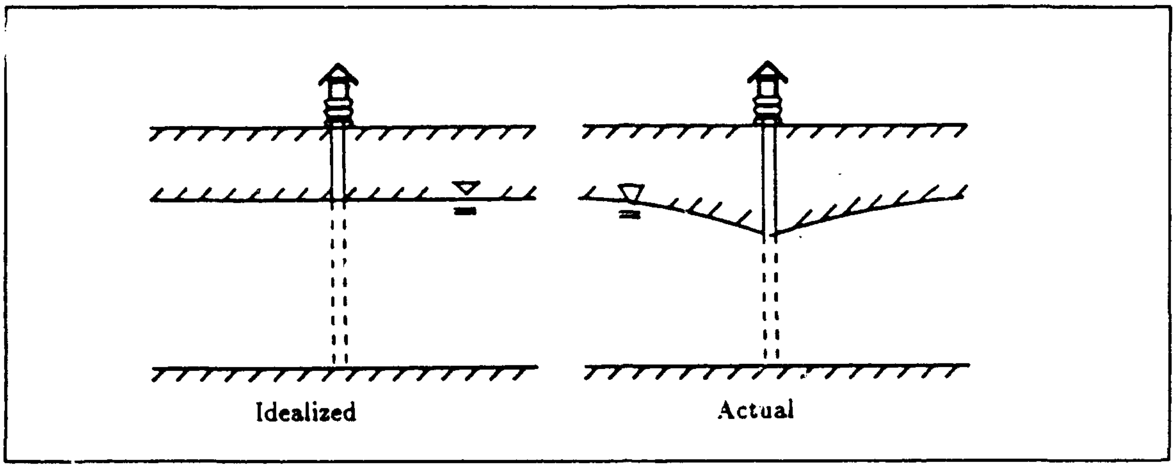

Figure 3.1. Drawdown assumption around a fully penetrating well in an aquifer (Huso, 1989: 1-4).

Secondly, the contamination is radially symmetric throughout the vertical extent of the aquifer. That is, a fully penetrating extraction well is placed in the center of a cylindrically symmetrical contaminated region (see Figure 3.2). It is also assumed that the concentration is finite, and no further contamination takes place from external sources or sinks of pollutant.

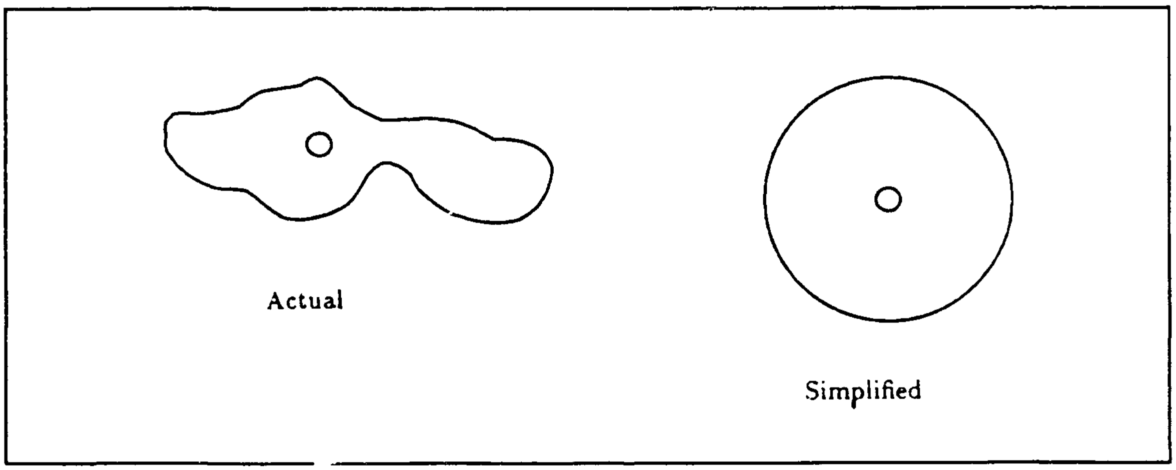

Figure 3.2. Radial symmetry of contaminant in comparison to real contaminant plume (Huso, 1989: 1-5).

The aquifer itself is assumed to be a single, infinite aquifer. This means the cone of depression will never intersect a boundary to the system and an infinite amount of water is stored in the aquifer (Domenico & Schwartz, 1990:151). The aquifer also is unconfined and considered to be of constant thickness bounded below a horizontal aquitard with no seepage. Likewise, homogeneity and isotropicity are assumed, implying that the transmissivity and storativity are constants in both space and time (Domenico & Schwartz, 1990:151).

Most importantly, the contaminant transport model utilized was based on the concept of rate-limited sorption/desorption within an aquifer. This was accomplished by dividing the porous medium into regions of mobile and immobile water, where advection and dispersion occurred in the mobile region and an additional equation was used to approximate the diffusional transfer of contaminant between the two regions (Adams & Viramontes, 1993:3-2). This first-order differential equation assumes that solute transfer between the mobile and immobile regions can be described by (Goltz & Oxley, 1991:548):

$$\frac{\partial C'_{im}(r,t)}{\partial t} = \frac{\alpha'}{\theta_{im} R_{im}}\left[C'_m(r,t) - C'_{im}(r,t)\right] \tag{3.1}$$

where it is assumed that the solute transfer is a function of the solute concentration difference between the mobile and immobile regions.

The assumptions made create a simplified aquifer while accounting for the often misrepresented phenomena of rate-limited sorption and together create an appropriate transport constraint for the optimization problem.

Class of Pumping Schedules. Due to the tailing phenomenon observed in aquifers affected by rate-limited sorption, pump-and-treat remediation has been criticized. This criticism evolves from the fact that large volumes of water are treated only to remove minimal amounts of contaminant at high cost and not necessarily to a health-based standard. Therefore an alternative method to resolve this problem is addressed, a pulsed pumping schedule, which allows desorption to occur during periods when the pumps are turned off. With this in mind, it is important to determine the class of pumping schedules or functions to be used.

The primary objective when formulating the optimization problem is to maximize or minimize a functional over some class of functions. In this thesis, the class of functions to be used will be the finite time horizon class,

$$\text{Let } t_{final} > 0 \text{ be a fixed finite time}$$

$$\text{Let } Q_{max} > 0 \text{ be a fixed finite pumping rate}$$

$$\text{Let } \mathcal{C} = \{ Q' : [0, t_{final}] \to \{0, Q_{max}\} \text{ and } Q' \text{ is piecewise constant} \}$$

Observe that the units of the pumping rate a Q' are $[L^3/T]$.

Objective Functionals

Functionals are a kind of function, where the independent variable is itself a function (Gelfand & Fomin, 1963:1). Calculus of variations utilizes the functional in order to find the maxima and minima through a variation of the functional. For this thesis, several objective functionals will be considered for their practicality. However, for this chapter a generalized form of the objective functional will be introduced. This general form can easily be substituted with specific objective functionals which can address management objectives, such as, minimizing pumping of water while maximizing contaminant extraction (i.e., optimize the pulsed-pumping method), minimize cost, maximize net economic return, minimize health and environmental effects, and minimize the time of cleanup to a health-based standard or federal mandate. By changing the objective functional one can apply the management tool described in this thesis for different scenarios.

Additionally, the objective functions described are presented in the form of integrals as opposed to summations. The first general functional in dimensional form is written as,

$$\int_0^{t_{final}} f'\left(t, Q'(t), C'_m(r_w, t)\right) dt \tag{3.2}$$

where

$C'_m(r_w, t)$	contaminant concentration in the mobile zone [M/L^3]
r_w	radial coordinate at the well [L]
t	time [T]
$Q'(t)$	pumping rate[L^3/T]
t_{final}	final fixed time [T]

and the functional in dimensionless form can be written as,

$$\int_0^{T_{final}} f\left(T, Q(T), C_m(X_w, T)\right) dT \tag{3.3}$$

where

$C_m(X_w, T)$	contaminant concentration in the mobile zone measured at the well which is equal to $\dfrac{C'_m(r_w, t)}{C'_o}$
X_w	radial coordinate at the well which is equal to $\dfrac{r_w}{a_1}$
T	time
$Q(T)$	pumping rate which is equal to $Q^{-1}_{max}Q'(t)$
T_{final}	final fixed time

Equation (3.3) will be used as the functional to be optimized.

For this discussion, Q(T) is a function whose values are 0 or 1. Also, due to the fact that the concentration of the contaminant in the mobile region, $C_m(X_w, T)$, depends on Q(T) from the contaminant transport equation and its boundary conditions, the objective functional is a nonlinear functional.

Constraints

Chapter 2 introduced the development of the differential equations for contaminant transport starting with the classical dispersion model in cylindrical coordinates and is given by the following equation (Valocchi, 1986:1693):

$$\frac{\partial C'(r,t)}{\partial t}+\frac{\rho}{\theta}\frac{\partial S(r,t)}{\partial t}=\frac{1}{r}\frac{\partial}{\partial r}\left[rD'\frac{\partial C'(r,t)}{\partial t}\right]-V'(r)\frac{\partial C'(r,t)}{\partial r} \tag{3.4}$$

where

$C'_m(r,t)$	contaminant concentration in the mobile zone [M/L^3]
r	radial coordinate [L]
t	time [T]
S(r,t)	sorbed contaminant [unitless]
$V'(r)$	seepage velocity [L/T]
ρ	bulk density of aquifer material [M/L^3]
θ	aquifer porosity [unitless]
D′	hydrodynamic dispersion coefficient [L^2/T]

and ended with the dimensional contaminant transport equation within the mobile region of a homogeneous, radially flowing aquifer incorporating both molecular and mechanical dispersion

$$\begin{aligned}\frac{\partial C'_m(r,t)}{\partial t}=&\frac{1}{R_m}\left(\frac{a_l Q'(t)}{2\pi b\theta_m r}+D^*\right)\frac{\partial^2 C'_m(r,t)}{\partial^2 r}+\frac{1}{R_m}\left(\frac{Q'(t)}{2\pi b\theta_m r}\right)\frac{\partial C'_m(r,t)}{\partial r}\\&+\frac{1}{R_m}\frac{1}{r}(D^*)\frac{\partial C'_m(r,t)}{\partial r}-\frac{\theta_{im}R_{im}}{\theta_m R_m}\frac{\partial C'_{im}(r,t)}{\partial t}\qquad r_w<r<\infty\end{aligned} \tag{3.5}$$

where

a_l	longitudinal dispersivity of the porous media [L]
D*	molecular diffusion constant
$C'_m(r,t)$	solute concentration in the mobile region [M/L^3]

$C'_{im}(r,t)$	volume-averaged immobile region solute concentration [M/L^3]
θ_m	mobile region porosity [unitless]
θ_{im}	immobile region porosity [unitless]
R_m	mobile region retardation factor [unitless]
R_{im}	immobile region retardation factor [unitless]
$Q'(t)$	extraction well pumping rate [L^3/T]
b	aquifer thickness [L]

In order to describe the transfer of solute between the mobile and immobile regions another equation is needed. A common model used is the first-order rate expression [Goltz & Oxley, 1991:548]:

$$\frac{\partial C'_{im}(r,t)}{\partial t} = \frac{\alpha'}{\theta_{im} R_{im}}\left(C'_m(r,t) - C'_{im}(r,t)\right) \qquad r_w < r < \infty \tag{3.6}$$

where this model assumes that the local concentration within the immobile regions are the same as the volume-averaged immobile region solute concentration (Goltz & Oxley, 1991,548).

Appendix A extends the derivation of both dimensional equations (3.5) and (3.6) which provide a more useful set of contaminant transport equations in a dimensionless form shown below:

$$\frac{\partial C_m(X,T)}{\partial T} = \left(\frac{Q(T)}{X} + D\right)\frac{\partial^2 C_m(X,T)}{\partial X^2} + \left(\frac{Q(T)}{X} + \frac{D}{X}\right)\frac{\partial C_m(X,T)}{\partial X} - \beta\frac{\partial C_{im}(X,T)}{\partial T} \tag{3.7}$$

and

$$\frac{\partial C_{im}(X,T)}{\partial T} = \alpha\left[C_m(X,T) - C_{im}(X,T)\right] \tag{3.8}$$

where the dimensionless variables are defined as

$$C_m(X,T) = \frac{C'_m(r,t)}{C'_o} \tag{3.9}$$

$$C_{im}(X,T)=\frac{C'_{im}(r,t)}{C'_o} \tag{3.10}$$

$$X=\frac{r}{a_1} \tag{3.11}$$

$$T=\frac{Q_{max}\,t}{2\pi b\,\theta_m\,a_1^{\,2}R_m} \tag{3.12}$$

and the dimensionless constants are

$$\alpha=\frac{2\pi b a_1^{\,2}\,\alpha'}{Q_{max}\,\beta} \tag{3.13}$$

$$D=\frac{2\pi b\,\theta_m\,D^{*}}{Q_{max}} \tag{3.14}$$

$$\beta=\frac{\theta_{im}\,R_{im}}{\theta_m\,R_m} \tag{3.15}$$

With the following initial conditions:

$$C_m(X,0)=C_{m,o}(X)=\begin{cases}1 & \text{for} \quad X_w<X<X_* \\ 0 & \text{for} \quad X_*<X<\infty\end{cases} \tag{3.16}$$

and

$$C_{im}(X,0)=C_{im,o}(X)=\begin{cases}1 & \text{for} \quad X_w<X<X_* \\ 0 & \text{for} \quad X_*<X<\infty\end{cases} \tag{3.17}$$

where $C_{m,0}(X)$ and $C_{im,0}(X)$ are dimensionless arbitrary initial conditions in the mobile region and immobile region and $X_*=\frac{r_*}{a_1}$ is some arbitrary finite radius which can approximate the extent of contamination. Also, the following boundary conditions are

$$\frac{\partial C_m}{\partial X}(\infty,T)+C_m(\infty,T)=0 \quad \text{and} \quad C_m(\infty,T)=0 \quad \text{for} \quad \text{all} \quad T\in[0,T_{final}] \tag{3.18}$$

and

$$\frac{\partial C_{im}}{\partial X}(\infty,T)+C_{im}(\infty,T)=0 \quad \text{and} \quad C_{im}(\infty,T)=0 \quad \text{for} \quad \text{all} \quad T\in[0,T_{final}] \tag{3.19}$$

where it is assumed that the total mass flux at the outer boundary ($X = \infty$) equals zero, since there is no contaminant mass at $X > X_*$ initially.

Laplace Transform. In this section a mathematical technique which is used in the solution of boundary-value problems is utilized. This technique is known as the Laplace transform, and it converts boundary-value problems involving linear differential equations as a function of time into an algebraic problem involving the Laplace transform variable (s) (Adams & Viramontes, 1993:3-2).

A general Laplace solution is derived from the transport equations (3.7) and (3.8) and combines these equations into one equation. A detailed derivation can be found in Appendix B. Taking the Laplace transform of equations (3.7) and (3.8), yields

$$\left(D+\frac{1}{X}\right)\frac{\partial^2 \overline{C}_m}{\partial X^2}+\left(\frac{D}{X}+\frac{1}{X}\right)\frac{\partial \overline{C}_m}{\partial X}-\gamma\,\overline{C}_m=\overline{F}(X,s) \qquad (3.20)$$

where the overbar indicates the corresponding transformed functions and

$$\overline{F}(X,s)=-\left(1+\frac{\beta s}{s+\alpha}\right)F(X) \qquad (3.21)$$

where $F(X) = C_{m,0}(X) = C_{im,0}(X)$ and

$$\gamma = s\left(\frac{\beta\alpha}{s+\alpha}+1\right) \qquad (3.22)$$

Lagrange Multipliers

In this section the concept of the constraint is introduced, where the Lagrange multiplier incorporates the contaminant transport equation with the calculus of variations approach. In calculus of variations, we want to find the maxima or minima of a quantity subject to a condition. This is were the Lagrange multiplier becomes useful. Often in physical problems, the variables of the objective functional are subjected to constraints and the Lagrange multiplier provides the vehicle to incorporate constraints into a new unconstrained optimization problem.

For this thesis the transport equation is an equality constraint (as a finite subsidiary condition) and the Lagrangian in differential form results in

$$\mathcal{L} = \int_0^{T_{final}} f(T, Q(T), C_m(X_w, T))\, dT + \int_0^{T_{final}} \int_{X_w}^{\infty} \lambda(X,T) \begin{bmatrix} G[C_m](X,T) + \beta\alpha e^{-\alpha T} C_{im,0}(X) \\ +\beta\alpha^2 e^{-\alpha T} \int_0^T e^{\alpha\tau} C_m(X,\tau)\, d\tau - \dfrac{\partial C_m}{\partial T} \end{bmatrix} dX dT \tag{3.23}$$

where $G[C_m]$ is defined to be the differential operator which depends on Q,

$$G[C_m](X,T) \equiv \left(\frac{Q(T)}{X} + D\right)\frac{\partial^2 C_m}{\partial X^2} + \left(\frac{Q(T)}{X} + \frac{D}{X}\right)\frac{\partial C_m}{\partial X} - \beta\alpha C_m \tag{3.24}$$

See Appendix E for a thorough formulation of the Lagrangian.

Formulation of the Optimization Problem

All of the elements to form the optimization problem have been discussed and rationalized. With the objective functionals, constraints, initial conditions and boundary conditions, the optimization problem can be formulated.

(1) State the problem:

Minimize $$\Im[Q] = \int_0^{T_{final}} f(T, Q(T), C_m(X_w, T))\, dT \tag{3.25}$$

over the piecewise constant set of functions $\mathcal{C} = \{ Q: [0, t_{final}] \rightarrow \{0, Q_{max}\}$ and Q is piecewise constant$\}$

(2) Subject to the constraints

$$\frac{\partial C_m(X,T)}{\partial T} = \left(\frac{Q(T)}{X} + D\right)\frac{\partial^2 C_m(X,T)}{\partial X^2} + \left(\frac{Q(T)}{X} + \frac{D}{X}\right)\frac{\partial C_m(X,T)}{\partial X} - \beta\frac{\partial C_{im}(X,T)}{\partial X} \tag{3.7}$$

and

$$\frac{\partial C_{im}(X,T)}{\partial T} = \alpha\left[C_m(X,T) - C_{im}(X,T)\right] \tag{3.8}$$

With the following initial conditions:

$$C_m(X,0) = C_{m,o}(X) = \begin{cases} 1 & \text{for} \quad X_w < X < X_* \\ 0 & \text{for} \quad X_* < X < \infty \end{cases} \tag{3.16}$$

and

$$C_{im}(X,0) = C_{im,o}(X) = \begin{cases} 1 & \text{for} \quad X_w < X < X_* \\ 0 & \text{for} \quad X_* < X < \infty \end{cases} \tag{3.17}$$

And the following boundary conditions

$$\frac{\partial C_m}{\partial X}(\infty,T) + C_m(\infty,T) = 0 \quad \text{and} \quad C_m(\infty,T) = 0 \quad \text{for} \quad \text{all} \quad T \in [0,T_{final}] \tag{3.18}$$

$$\frac{\partial C_{im}}{\partial X}(\infty,T) + C_{im}(\infty,T) = 0 \quad \text{and} \quad C_{im}(\infty,T) = 0 \quad \text{for} \quad \text{all} \quad T \in [0,T_{final}] \tag{3.19}$$

Necessary Optimality Conditions for the First Variation

Recalling that derivatives give slopes so you may find maximum and minimum points of $y = f(x)$ by setting $dy/dx = 0$, we can extend this concept to find the maxima and minima of functions of more than one variable. For example, if there is a maximum or minimum point for the function $z = f(x, y)$, then the necessary but not sufficient condition is that $\frac{\partial z}{\partial x} = 0$ and $\frac{\partial z}{\partial y} = 0$ whereupon the point may be a maximum point, minimum point or neither (Boas, 1983:169).

Often in applied problems we find the maxima or minima of functions of more than one variable subject to a constraint. To solve such problems we can use the method of Lagrange multipliers or undetermined multipliers, which is stated below

> To find the maximum or minimum values of $f(x, y)$ when x and y are related by the equation $\phi(x,y)=$ constant, form the function
>
> $$F(x,y) = f(x,y) + \lambda\phi(x,y)$$
>
> and set the two partial derivatives of F equal to zero, i.e.,
>
> $$\frac{\partial f}{\partial y} + \lambda\frac{\partial f}{\partial y} = 0 \text{ and } \frac{\partial f}{\partial x} + \lambda\frac{\partial f}{\partial x} = 0$$
>
> Then solve these two equations and the equation $\phi(x, y) =$ constant for the three unknowns x, y, and λ (Boas, 1983: 175).

This motivates the concept of the variation (or differential) of a functional, which is analogous to the concept of the differential of a function of n variables (Gelfand & Fomin, 1963: 8). Additionally, this type of optimal control can be related to the calculus of variations, where the optimal control is a variance of the problem to finding a critical point (i.e., minimum, maximum or saddle point) subject to subsidiary conditions as discussed earlier (Gelfand & Fomin, 1963: 8).

Constructing the first variation. Recalling the Lagrangian in differential form, equation (3.23)

$$\mathcal{L}[Q,C_m,\lambda] = \int_0^{T_{final}} f(T,Q(T),C_m(X_w,T))\,dT + \int_0^{T_{final}}\int_{X_w}^{\infty} \lambda(X,T)\begin{bmatrix} G[C_m](X,T) + \beta\alpha e^{-\alpha T} C_{im,0}(X) \\ +\beta\alpha^2 e^{-\alpha T}\int_0^T e^{\alpha\tau} C_m(X,\tau)\,d\tau - \dfrac{\partial C_m}{\partial T}\end{bmatrix} dX\,dT \tag{3.23}$$

and noting that the contaminant transport constraint is

$$\frac{\partial C_m(X,T)}{\partial T} = \left(\frac{Q(T)}{X} + D\right)\frac{\partial^2 C_m}{\partial X^2} + \left(\frac{Q(T)}{X} + \frac{D}{X}\right)\frac{\partial C_m}{\partial X} - \beta\alpha C_m + \beta\alpha e^{-\alpha T} C_{im,0}(X) + \beta\alpha^2 e^{-\alpha T}\int_0^T e^{\alpha\tau} C_m(X,\tau)\,d\tau \tag{3.26}$$

or

$$0 = \left(\frac{Q(T)}{X} + D\right)\frac{\partial^2 C_m}{\partial X^2} + \left(\frac{Q(T)}{X} + \frac{D}{X}\right)\frac{\partial C_m}{\partial X} - \beta\alpha C_m + \beta\alpha e^{-\alpha T} C_{im,0}(X) + \beta\alpha^2 e^{-\alpha T}\int_0^T e^{\alpha\tau} C_m(X,\tau)\,d\tau - \frac{\partial C_m(X,T)}{\partial T} \tag{3.27}$$

where equation (3.27) has six terms which can be simplified by performing integration by parts on each term (see Appendix E for a detailed derivation). Results in the equivalent Lagrangian

$$
\begin{aligned}
\mathcal{L} &= \int_0^{T_{final}} f(T, Q(T), C_m(X_w, T))\,dT \\
&+ \int_0^{T_{final}} \int_{X_w}^{\infty} C_m(X,T) \left\{ \begin{aligned} &\frac{\partial \lambda}{\partial T}(X,T) + \frac{\partial^2}{\partial X^2}\left[\lambda(X,T)\left(\frac{Q(T)}{X} + D\right)\right] - \frac{\partial}{\partial X}\left[\lambda(X,T)\left(\frac{Q(T)}{X} + \frac{D}{X}\right)\right] \\ &-\beta\alpha\lambda(X,T) + \alpha^2\beta e^{\alpha T}\int_T^{T_{final}} e^{-\alpha t}\lambda(X,t)\,dt \end{aligned} \right\} dX dT \\
&+ \int_0^{T_{final}} \int_{X_w}^{\infty} \beta\alpha e^{-\alpha T}\lambda(X,T) C_{m,0}(X)\,dX dT \\
&- \int_0^{T_{final}} D C_m(\infty, T)\left[\lambda(\infty, T) + \frac{\partial \lambda}{\partial X}(\infty, T)\right] dT \\
&+ \int_0^{T_{final}} C_m(X_w, T)\left\{\frac{\partial \lambda}{\partial X}(X_w, T)\left(\frac{Q(T)}{X_w} + D\right) - \lambda(X_w, T)\left(\frac{Q(T)}{X_w} + \frac{D}{X_w}\right) - \lambda(X_w, T)\frac{Q(T)}{X_w^{\ 2}}\right\} dT \\
&- \int_{X_w}^{\infty} \lambda(X, T_{final}) C_m(X, T_{final})\,dX + \int_{X_w}^{\infty} \lambda(X, 0) C_{m,0}(X)\,dX
\end{aligned}
$$

(3.28)

First Variation. With the Lagrangian in two forms both the abbreviated version equation (3.23) and the expanded version equation (3.28) and noting that the Lagrangian is subject to various constraints, we next take the variation of the Lagrangian with respect to each variable i.e., C_m, λ ,and Q starting with the variation of $\mathcal{L}$ with respect to C_m where:

$$\delta\mathcal{L}[Q, C_m, \lambda; 0, h, 0] = \lim_{a \to 0} \frac{d}{da} \mathcal{L}[Q, C_m + ah, \lambda] \qquad (3.29)$$

which is

$$\delta\mathcal{L}[Q, C_m, \lambda; 0, h, 0] = \int_0^{T_{final}} \frac{\partial f}{\partial C}[T, Q(T), C_m(X_w, T)] h(X_w, T)\, dT$$

$$+\int_0^{T_{final}} \int_{X_w}^{\infty} h(X,T) \left\{ \begin{array}{l} \dfrac{\partial \lambda}{\partial T}(X,T) + \dfrac{\partial^2}{\partial X^2}\left[\lambda(X,T)\left(\dfrac{Q(T)}{X} + D\right)\right] - \dfrac{\partial}{\partial X}\left[\lambda(X,T)\left(\dfrac{Q(T)}{X} + \dfrac{D}{X}\right)\right] \\ -\beta\alpha\lambda(X,T) + \alpha^2 \beta e^{\alpha T} \int_T^{T_{final}} e^{-\alpha t} \lambda(X,t)\, dt \end{array} \right\} dX dT$$

$$-\int_0^{T_{final}} D h(\infty, T)\left[\lambda(\infty, T) + \frac{\partial \lambda}{\partial X}(\infty, T)\right] dT$$

$$+\int_0^{T_{final}} h(X_w, T)\left\{\frac{\partial \lambda}{\partial X}(X_w, T)\left(\frac{Q(T)}{X_w} + D\right) - \lambda(X_w, T)\left(\frac{Q(T)}{X_w} + \frac{D}{X_w}\right) - \lambda(X_w, T)\frac{Q(T)}{X_w^{\ 2}}\right\} dT$$

$$-\int_{X_w}^{\infty} \lambda(X, T_{final}) h(X, T_{final})\, dX$$

(3.30)

Next we take the variation of $\mathcal{L}$ with respect to λ using equation (3.23). For a detailed evaluation (see Appendix E).

$$\delta\mathcal{L}[Q, C_m, \lambda; 0, 0, \mu] = \lim_{a \to 0} \frac{d}{da} \mathcal{L}[Q, C_m, \lambda + a\,\mu] \qquad (3.31)$$

which yields

$$\delta\mathcal{L}[Q, C_m, \lambda; 0, 0, \mu] =$$

$$\int_0^{T_{final}} \int_{X_w}^{\infty} \mu(X,T)\left[G[C_m] + \beta\alpha e^{-\alpha T} C_{im,0}(X) + \beta\alpha^2 e^{-\alpha T} \int_0^T e^{\alpha\tau} C_m(X,\tau)\, d\tau - \frac{\partial C_m}{\partial T}\right] dX dT$$

(3.32)

Lastly, we take the variation of $\mathcal{L}$ with respect to Q. This is equivalent to the derivative of $\mathcal{L}$ with respect to time. But first we rewrite equation (3.28) where Q(T) represents pulsed pumping and Q(T) = 1 when evaluated between $0 < T < T_1$, Q(T) = 0 when evaluated between $T_1 < T < T_2$, and $Q(T) = 1$ when evaluated between $T_2 < T < T_3$ where $T_3 = T_{final}$. Here T_1 and T_2 are variabies.

Define $C_m^{(i)}$ for $i = 1, 2, 3$ by

$$C_m(X,T) = \begin{cases} C_m^{(1)}(X,T) & \text{for} \quad 0 \le T \le T_1 \\ C_m^{(2)}(X,T) & \text{for} \quad T_1 < T \le T_2 \\ C_m^{(3)}(X,T) & \text{for} \quad T_2 < T \le T_3 \end{cases} \tag{3.33}$$

Similarly, define $\lambda^{(i)}$ for $i = 1, 2, 3$ by

$$\lambda(X,T) = \begin{cases} \lambda^{(1)}(X,T) & \text{for} \quad 0 \le T \le T_1 \\ \lambda^{(2)}(X,T) & \text{for} \quad T_1 < T \le T_2 \\ \lambda^{(3)}(X,T) & \text{for} \quad T_2 < T \le T_3 \end{cases} \tag{3.34}$$

Additionally, in general we define the adjoint differential operator as

$$G^*[\lambda](X,T) \equiv \frac{\partial^2}{\partial X^2}\left[\left(\frac{Q(T)}{X} + D\right)\lambda\right] - \frac{\partial}{\partial X}\left[\left(\frac{Q(T)}{X} + \frac{D}{X}\right)\lambda\right] - \alpha\beta\lambda \tag{3.35}$$

Specifically, when the pump is on the adjoint differential operator is

$$G^*_{on}[\lambda](X,T) \equiv \frac{\partial^2}{\partial X^2}\left[\left(\frac{1}{X} + D\right)\lambda\right] - \frac{\partial}{\partial X}\left[\left(\frac{1}{X} + \frac{D}{X}\right)\lambda\right] - \alpha\beta\lambda \tag{3.36}$$

and when the pump is off the adjoint differential operator is

$$G^*_{off}[\lambda](X,T) \equiv \frac{\partial^2}{\partial X^2}[D\lambda] - \frac{\partial}{\partial X}\left[\frac{D}{X}\lambda\right] - \alpha\beta\lambda \tag{3.37}$$

results in

$$
\begin{aligned}
\mathcal{L} = &\int_0^{T_1} f\left[T,1,C_m^{(1)}(X_w,T)\right]dT - \int_{T_1}^{T_2} f\left[T,0,C_m^{(2)}(X_w,T)\right]dT + \int_{T_2}^{T_3} f\left[T,1,C_m^{(3)}(X_w,T)\right]dT \\
&+\int_0^{T_1}\int_{X_w}^{\infty} C_m^{(1)}(X,T)\left\{\frac{\partial\lambda^{(1)}}{\partial T}(X,T) + G_{on}^{*}\left[\lambda^{(1)}\right](X,T) + \alpha^2\beta e^{\alpha T}\left[\begin{array}{l}\int_T^{T_1} e^{-\alpha t}\lambda^{(1)}(X,t)\,dt + \int_{T_1}^{T_2} e^{-\alpha t}\lambda^{(2)}(X,t)\,dt \\ +\int_{T_2}^{T_3} e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\end{array}\right]\right\}dXdT \\
&+\int_{T_1}^{T_2}\int_{X_w}^{\infty} C_m^{(2)}(X,T)\left\{\frac{\partial\lambda^{(2)}}{\partial T}(X,T) + G_{off}^{*}\left[\lambda^{(2)}\right](X,T) + \alpha^2\beta e^{\alpha T}\left[\int_T^{T_2} e^{-\alpha t}\lambda^{(2)}(X,t)\,dt + \int_{T_2}^{T_3} e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\right]\right\}dXdT \\
&+\int_{T_2}^{T_3}\int_{X_w}^{\infty} C_m^{(3)}(X,T)\left\{\frac{\partial\lambda^{(3)}}{\partial T}(X,T) + G_{on}^{*}\left[\lambda^{(3)}\right](X,T) + \alpha^2\beta e^{\alpha T}\int_T^{T_3} e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\right\}dXdT \\
&-\int_0^{T_1} DC_m^{(1)}(\infty,T)\left[\lambda^{(1)}(\infty,T) + \frac{\partial\lambda^{(1)}}{\partial X}(\infty,T)\right]dT - \int_{T_1}^{T_2} DC_m^{(2)}(\infty,T)\left[\lambda^{(2)}(\infty,T) + \frac{\partial\lambda^{(2)}}{\partial X}(\infty,T)\right]dT \\
&-\int_{T_2}^{T_3} DC_m^{(3)}(\infty,T)\left[\lambda^{(3)}(\infty,T) + \frac{\partial\lambda^{(3)}}{\partial X}(\infty,T)\right]dT \\
&+\int_0^{T_1} C_m^{(1)}(X_w,T)\left\{\frac{\partial\lambda^{(1)}}{\partial X}(X_w,T)\left(\frac{1}{X_w}+D\right) - \lambda^{(1)}(X_w,T)\left(\frac{1}{X_w}+\frac{D}{X_w}\right) - \lambda^{(1)}(X_w,T)\frac{1}{X_w^{\,2}}\right\}dT \\
&+\int_{T_1}^{T_2} C_m^{(2)}(X_w,T)\left\{\frac{\partial\lambda^{(2)}}{\partial X}(X_w,T)D - \lambda^{(2)}(X_w,T)\frac{D}{X_w}\right\}dT \\
&+\int_{T_2}^{T_3} C_m^{(3)}(X_w,T)\left\{\frac{\partial\lambda^{(3)}}{\partial X}(X_w,T)\left(\frac{1}{X_w}+D\right) - \lambda^{(3)}(X_w,T)\left(\frac{1}{X_w}+\frac{D}{X_w}\right) - \lambda^{(3)}(X_w,T)\frac{1}{X_w^{\,2}}\right\}dT \\
&-\int_{X_w}^{\infty} \lambda^{(3)}(X,T_{final})C_m^{(3)}(X,T)\,dX
\end{aligned}
\tag{3.38}
$$

Taking the variation (i.e., derivative) of $\mathcal{L}$ with respect to T_1 results in

$$
\begin{aligned}
\frac{\partial}{\partial T_1}\mathcal{L} = &f\left[T_1,1,C_m^{(1)}(X_w,T_1)\right] - f\left[T_1,0,C_m^{(2)}(X_w,T_1)\right] \\
&+\int_{X_w}^{\infty} C_m^{(1)}(X,T_1)\left\{\frac{\partial\lambda^{(1)}}{\partial T}(X,T_1) + G_{on}^{*}\left[\lambda^{(1)}\right](X,T_1) + \alpha^2\beta e^{\alpha T_1}\left[\int_{T_1}^{T_2} e^{-\alpha t}\lambda^{(2)}(X,t)\,dt + \int_{T_2}^{T_3} e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\right]\right\}dX \\
&-\int_{X_w}^{\infty} C_m^{(2)}(X,T_1)\left\{\frac{\partial\lambda^{(2)}}{\partial T}(X,T_1) + G_{off}^{*}\left[\lambda^{(2)}\right](X,T_1) + \alpha^2\beta e^{\alpha T_1}\left[\int_{T_1}^{T_2} e^{-\alpha t}\lambda^{(2)}(X,t)\,dt + \int_{T_2}^{T_3} e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\right]\right\}dX \\
&-DC_m^{(1)}(\infty,T_1)\left[\lambda^{(1)}(\infty,T_1) + \frac{\partial\lambda^{(1)}}{\partial X}(\infty,T_1)\right] + DC_m^{(2)}(\infty,T_1)\left[\lambda^{(2)}(\infty,T_1) + \frac{\partial\lambda^{(2)}}{\partial X}(\infty,T_1)\right]
\end{aligned}
$$

$$+C_m^{(1)}(X_w,T_1)\left\{\frac{\partial\lambda^{(1)}}{\partial X}(X_w,T_1)\left(\frac{1}{X_w}+D\right)-\lambda^{(1)}(X_w,T_1)\left(\frac{1}{X_w}+\frac{D}{X_w}\right)-\lambda^{(1)}(X_w,T_1)\frac{1}{X_w^{\;2}}\right\}$$
$$-C_m^{(2)}(X_w,T_1)\left\{\frac{\partial\lambda^{(2)}}{\partial X}(X_w,T_1)D-\lambda^{(2)}(X_w,T_1)\frac{D}{X_w}\right\}$$

(3.39)

Taking the variation (i.e., derivative) of $\mathcal{L}$ with respect to T_2 results in

$$\frac{\partial}{\partial T_2}\mathcal{L}=f\left[T_2,0,C_m^{(2)}(X_w,T_2)\right]-f\left[T_2,1,C_m^{(3)}(X_w,T_2)\right]$$
$$+\int_{X_w}^{\infty}C_m^{(2)}(X,T_2)\left\{\frac{\partial\lambda^{(2)}}{\partial T}(X,T_2)+G_{off}^{*}\left[\lambda^{(2)}\right](X,T_2)+\alpha^2\beta e^{\alpha T_2}\int_{T_2}^{T_3}e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\right\}dX$$
$$-\int_{X_w}^{\infty}C_m^{(3)}(X,T_2)\left\{\frac{\partial\lambda^{(3)}}{\partial T}(X,T_2)+G_{on}^{*}\left[\lambda^{(3)}\right](X,T_2)+\alpha^2\beta e^{\alpha T_2}\int_{T_2}^{T_3}e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\right\}dX$$
$$-DC_m^{(2)}(\infty,T_2)\left[\lambda^{(2)}(\infty,T_2)+\frac{\partial\lambda^{(2)}}{\partial X}(\infty,T_2)\right]+DC_m^{(3)}(\infty,T_2)\left[\lambda^{(3)}(\infty,T_2)+\frac{\partial\lambda^{(3)}}{\partial X}(\infty,T_2)\right]$$
$$+C_m^{(2)}(X_w,T_2)\left\{\frac{\partial\lambda^{(2)}}{\partial X}(X_w,T_2)D-\lambda^{(2)}(X_w,T_2)\frac{D}{X_w}\right\}$$
$$-C_m^{(3)}(X_w,T_2)\left\{\frac{\partial\lambda^{(3)}}{\partial X}(X_w,T_2)\left(\frac{1}{X_w}+D\right)-\lambda^{(3)}(X_w,T_2)\left(\frac{1}{X_w}+\frac{D}{X_w}\right)-\lambda^{(3)}(X_w,T_2)\frac{1}{X_w^{\;2}}\right\}$$

(3.40)

Application of the Necessary Optimality Condition for the First Variation. Using the variations of the Lagrangian with respect to each variable (i.e., C_m, λ, and Q) we can determine the necessary optimality condition for the first variation applied to $\mathcal{L}$. Since the functional described in this thesis yields a linear functional for the first variation, we can introduce and utilize the following Lemmas:

Lemma 1. *If* A(T) *is continuous in* [a,b], *and if*

$$\int_a^b A(T)\,h(T)\,dT=0$$

for every function h *which is continuous* on [a,b] *such that* h(a) = h(b) = 0, *then* A(T) = 0 *for all* $T\in[a,b]$ (Gelfand & Fomin, 1963:9).

and

Lemma 2. *Let* R = [a,b] x [c,d]. *If* A(X,T) *is continuous in* R *and if*

$$\int_a^b A(X,T)\,h(X,T)\,dXdT = 0$$

for every function h *which is continuous on* R *such that* h(x,y) = 0 *for* (x,y) $\in \partial$R, *then* A(x,y) = 0 *for all* (x,y) $\in$ R (Gelfand & Fomin, 1963:9).

The necessary conditions for optimality to the first variation of $\mathcal{L}$ with respect to C_m will be applied. Suppose $\hat{C}_m$ minimizes $\mathcal{L}$ then necessarily $\delta\mathcal{L}\left[Q,\hat{C}_m,\lambda;0,h,0\right]=0$ for all admissible variations h.

Case 1.1:

Choose h such that

$$h(X,T) = 0 \text{ for all } X\in[X_w,\infty) \text{ and } T\in[T_1,T_3]$$

$$h(X,0) = 0 \text{ for all } X\in[X_w,\infty)$$

$$h(X_w,T) = 0 \text{ for all } T\in[0,T_1]$$

$$h(\infty,T) = 0 \text{ for all } T\in[0,T_1]$$

then equation (3.30) becomes

$$\delta\mathcal{L}\left[Q,\hat{C}_m,\lambda;0,h,0\right]=$$

$$\int_0^{T_1}\int_{X_w}^{\infty} h^{(1)}(X,T)\left\{\begin{aligned}&\frac{\partial\lambda^{(1)}}{\partial T}(X,T)+G^{*}_{on}\left[\lambda^{(1)}\right](X,T)\\&+\beta\alpha^2e^{\alpha T}\left[\begin{aligned}&\int_T^{T_1}e^{-\alpha t}\lambda^{(1)}(X,t)\,dt+\int_{T_1}^{T_2}e^{-\alpha t}\lambda^{(2)}(X,t)\,dt\\&+\int_{T_2}^{T_3}e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\end{aligned}\right]\end{aligned}\right\}dXdT=0 \tag{3.41}$$

Applying Lemma 2 to equation (3.41) produces the necessary optimality condition,

$$\frac{\partial\lambda^{(1)}}{\partial T}(X,T)+G_{\infty}^{*}\left[\lambda^{(1)}\right](X,T)+\beta\alpha^{2}e^{\alpha T}\left[\begin{array}{l}\int_{T}^{T_1}e^{-\alpha t}\lambda^{(1)}(X,t)\,dt+\int_{T_1}^{T_2}e^{-\alpha t}\lambda^{(2)}(X,t)\,dt\\+\int_{T_2}^{T_3}e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\end{array}\right]=0 \tag{3.42}$$

for all $X\in[X_w,\infty)$ and $T\in[0,T_1]$.

Case 1.2:

Choose h such that

$$h(X,T)=0 \text{ for all } X\in[X_w,\infty) \text{ and } T\in[T_1,T_3]$$

$$h(X,0)=0 \text{ for all } X\in[X_w,\infty)$$

$$h(X_w,T)\neq 0 \text{ for all } T\in(0,T_1)$$

$$h(\infty,T)=0 \text{ for all } T\in[0,T_1]$$

then equation (3.30) becomes

$$\begin{aligned}\delta\ell\left[Q,\hat{C}_m,\lambda;0,h,0\right]&=\int_0^{T_1}\frac{\partial f}{\partial C}\left[T,Q(T),\hat{C}_m^{(1)}(X_w,T)\right]h^{(1)}(X_w,T)\,dT\\&+\int_0^{T_1}h^{(1)}(X_w,T)\left\{\frac{\partial\lambda^{(1)}}{\partial X}(X_w,T)\left(\frac{1}{X_w}+D\right)-\lambda^{(1)}(X_w,T)\left(\frac{1}{X_w}+\frac{D}{X_w}\right)-\lambda^{(1)}(X_w,T)\frac{1}{X_w^2}\right\}dT=0\end{aligned} \tag{3.43}$$

Applying Lemma 1 to equation (3.43) produces the necessary optimality condition,

$$\begin{aligned}&\frac{\partial f}{\partial C}\left[T,Q(T),\hat{C}_m^{(1)}(X_w,T)\right]+\\&\left\{\frac{\partial\lambda^{(1)}}{\partial X}(X_w,T)\left(\frac{1}{X_w}+D\right)-\lambda^{(1)}(X_w,T)\left(\frac{1}{X_w}+\frac{D}{X_w}\right)-\lambda^{(1)}(X_w,T)\frac{1}{X_w^2}\right\}=0\end{aligned} \tag{3.44}$$

for all $T\in\left[0,T_1\right]$.

Case 1.3:

Choose h such that

$$h(X,T)=0 \text{ for all } X\in[X_w,\infty) \text{ and } T\in[T_1,T_3]$$

$$h(X,0) = 0 \text{ for all } X \in [X_w, \infty)$$

$$h(X_w, T) = 0 \text{ for all } T \in [0, T_1]$$

$$h(\infty, T) \neq 0 \text{ for all } T \in (0, T_1)$$

then equation (3.30) becomes

$$\delta\ell\left[Q, \hat{C}_m, \lambda; 0, h, 0\right] = -\int_0^{T_1} Dh^{(1)}(\infty, T)\left\{\lambda^{(1)}(\infty, T) + \frac{\partial\lambda^{(1)}}{\partial X}(\infty, T)\right\} dT = 0 \tag{3.45}$$

Applying Lemma 1 to equation (3.45) produces the necessary optimality condition,

$$\lambda^{(1)}(\infty, T) + \frac{\partial\lambda^{(1)}}{\partial X}(\infty, T) = 0 \tag{3.46}$$

for all $T \in [0, T_1]$.

<u>Case 2.1:</u>

Choose h such that

$$h(X,T) = 0 \text{ for all } T \in [0, T_1] \cup [T_2, T_3] \text{ and } X \in [X_w, \infty)$$

$$h(X_w, T) = 0 \text{ for all } T \in [T_1, T_2]$$

$$h(\infty, T) = 0 \text{ for all } T \in [T_1, T_2]$$

then equation (3.30) becomes

$$\delta\ell\left[Q, \hat{C}_m, \lambda; 0, h, 0\right] = \int_{T_1}^{T_2}\int_{X_w}^{\infty} h^{(2)}(X,T)\left\{\begin{array}{l} \dfrac{\partial\lambda^{(2)}}{\partial T}(X,T) + G^{*}_{\text{off}}\left[\lambda^{(2)}\right](X,T) \\ +\beta\alpha^2 e^{\alpha T}\left[\begin{array}{l} \int_T^{T_2} e^{-\alpha t}\lambda^{(2)}(X,t)\,dt \\ +\int_{T_2}^{T_3} e^{-\alpha t}\lambda^{(3)}(X,t)\,dt \end{array}\right] \end{array}\right\} dX\,dT = 0 \tag{3.47}$$

Applying Lemma 2 to equation (3.47) produces the necessary optimality condition,

$$\frac{\partial\lambda^{(2)}}{\partial T}(X,T)+G^{*}_{off}\left[\lambda^{(2)}\right](X,T)+\beta\alpha^{2}e^{\alpha T}\left[\int_{T}^{T_2}e^{-\alpha t}\lambda^{(2)}(X,t)\,dt+\int_{T_2}^{T_3}e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\right]=0 \tag{3.48}$$

for all $X \in [X_w, \infty)$ and $T \in [T_1, T_2]$.

Case 2.2:

Choose h such that

$$h(X,T) = 0 \text{ for all } T \in [0,T_1] \cup [T_2,T_3] \text{ and } X \in [X_w, \infty)$$

$$h(X_w,T) \neq 0 \text{ for all } T \in (T_1,T_2)$$

$$h(\infty,T) = 0 \text{ for all } T \in [T_1,T_2]$$

then equation (3.30) becomes

$$\begin{aligned}\delta\ell\left[Q,\hat{C}_m,\lambda;0,h,0\right] &= \int_{T_1}^{T_2}\frac{\partial f}{\partial C}\left[T,Q(T),\hat{C}^{(2)}_m(X_w,T)\right]h^{(2)}(X_w,T)\,dT \\ &+\int_{T_1}^{T_2}h^{(2)}(X_w,T)\left\{\frac{\partial\lambda^{(2)}}{\partial X}(X_w,T)D-\lambda^{(2)}(X_w,T)\frac{D}{X_w}\right\}dT=0\end{aligned} \tag{3.49}$$

Applying Lemma 1 to equation (3.49) produces the necessary optimality condition,

$$\frac{\partial f}{\partial C}\left[T,Q(T),\hat{C}^{(2)}_m(X_w,T)\right]+D\left\{\frac{\partial\lambda^{(2)}}{\partial X}(X_w,T)D-\lambda^{(2)}(X_w,T)\frac{D}{X_w}\right\}=0 \tag{3.50}$$

r all $T \in [T_1, T_2]$.

Case 2.3:

Choose h such that

$$h(X,T) = 0 \text{ for all } T \in [0,T_1] \cup [T_2,T_3] \text{ and } X \in [X_w, \infty)$$

$$h(X_w,T) = 0 \text{ for all } T \in [T_1,T_2]$$

$$h(\infty,T) \neq 0 \text{ for all } T \in (T_1,T_2)$$

then equation (3.30) becomes

$$\delta\ell\left[Q,\hat{C}_m,\lambda;0,h,0\right] = -\int_{T_1}^{T_2} Dh^{(2)}(\infty,T)\left\{\lambda^{(2)}(\infty,T)+\frac{\partial\lambda^{(2)}}{\partial X}(\infty,T)\right\}dT = 0 \tag{3.51}$$

Applying Lemma 1 to equation (3.51) produces the necessary optimality condition,

$$\lambda^{(2)}(\infty,T)+\frac{\partial\lambda^{(2)}}{\partial X}(\infty,T) = 0 \tag{3.52}$$

for all $T \in [T_1, T_2]$.

Case 3.1:

Choose h such that

$$h(X,T) = 0 \text{ for all } X \in [X_w,\infty) \text{ and } T \in [0,T_2]$$

$$h(X_w,T) = 0 \text{ for all } T \in [T_2,T_3]$$

$$h(\infty,T) = 0 \text{ for all } T \in [T_2,T_3]$$

$$h(X,T_3) = 0 \text{ for all } X \in [X_w,\infty)$$

then equation (3.30) becomes

$$\delta\ell\left[Q,\hat{C}_m,\lambda;0,h,0\right] = \int_{T_2}^{T_3}\int_{X_w}^{\infty} h^{(3)}(X,T)\left\{\begin{aligned}&\frac{\partial\lambda^{(3)}}{\partial T}(X,T)+G_{on}^{*}\left[\lambda^{(3)}\right](X,T)\\ &+\beta\alpha^2 e^{\alpha T}\int_T^{T_3} e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\end{aligned}\right\}dXdT = 0 \tag{3.53}$$

Applying Lemma 2 to equation (3.53) produces the necessary optimality condition,

$$\frac{\partial\lambda^{(3)}}{\partial T}(X,T)+G_{on}^{*}\left[\lambda^{(3)}\right](X,T)+\beta\alpha^2 e^{\alpha T}\int_T^{T_3} e^{-\alpha t}\lambda^{(3)}(X,t)\,dt = 0 \tag{3.54}$$

For all $X \in [Xw,\infty)$ and $T \in [T_2,T_3]$.

Case 3.2:

Choose h such that

$$h(X,T) = 0 \text{ for all } X \in [X_w, \infty) \text{ and } T \in [0, T_2]$$

$$h(X_w, T) \neq 0 \text{ for all } T \in (T_2, T_3)$$

$$h(\infty, T) = 0 \text{ for all } T \in [T_2, T_3]$$

$$h(X, T_3) = 0 \text{ for all } X \in [X_w, \infty)$$

then equation (3.30) becomes

$$\delta\ell\left[Q, \hat{C}_m, \lambda; 0, h, 0\right] = \int_{T_2}^{T_3} \frac{\partial f}{\partial C}\left[T, Q(t), \hat{C}_m^{(3)}(X_w, T)\right] h^{(3)}(X_w, T)\, dT$$
$$+ \int_{T_2}^{T_3} h^{(3)}(X_w, T) \left\{ \frac{\partial \lambda^{(3)}}{\partial X}(X_w, T)\left(\frac{1}{X_w} + D\right) - \lambda^{(3)}(X_w, T)\left(\frac{1}{X_w} + \frac{D}{X_w}\right) - \lambda^{(3)}(X_w, T)\frac{1}{X_w^2} \right\} dT = 0 \tag{3.55}$$

Applying Lemma 1 to equation (3.55) produces the necessary optimality condition,

$$\frac{\partial f}{\partial C}\left[T, Q(t), \hat{C}_m^{(3)}(X_w, T)\right] + \left\{ \begin{aligned} &\frac{\partial \lambda^{(3)}}{\partial X}(X_w, T)\left(\frac{1}{X_w} + D\right) \\ &-\lambda^{(3)}(X_w, T)\left(\frac{1}{X_w} + \frac{D}{X_w}\right) - \lambda^{(3)}(X_w, T)\frac{1}{X_w^2} \end{aligned} \right\} = 0 \tag{3.56}$$

for all $T \in [T_2, T_3]$.

Case 3.3:

Choose h such that

$$h(X,T) = 0 \text{ for all } X \in [X_w, \infty) \text{ and } T \in [0, T_2]$$

$$h(X_w, T) = 0 \text{ for all } T \in [T_2, T_3]$$

$$h(\infty, T) \neq 0 \text{ for all } T \in (T_2, T_3)$$

$$h(X, T_3) = 0 \text{ for all } X \in [X_w, \infty)$$

then equation (3.30) becomes

$$\delta\mathcal{L}\left[Q,\hat{C}_m,\lambda;0,h,0\right]=-\int_{T_2}^{T_3}Dh^{(3)}(\infty,T)\left\{\lambda^{(3)}(\infty,T)+\frac{\partial\lambda^{(3)}}{\partial X}(\infty,T)\right\}dT=0 \tag{3.57}$$

Applying Lemma 1 to equation (3.57) produces the necessary optimality condition,

$$\lambda^{(3)}(\infty,T)+\frac{\partial\lambda^{(3)}}{\partial X}(\infty,T)=0 \tag{3.58}$$

for all $T\in\left[T_2,T_3\right]$.

<u>Case 3.4:</u>

Choose h such that

$$h(X,T) = 0 \text{ for all } X \in [X_w,\infty) \text{ and } T\in\left[0,T_2\right]$$

$$h(X_w,T) = 0 \text{ for all } T\in[T_2,T_3]$$

$$h(\infty,T) = 0 \text{ for all } T\in[T_2,T_3]$$

$$h(X, T_3) \neq 0 \text{ for all } X \in (X_w,\infty)$$

then equation (3.30) becomes

$$\delta\mathcal{L}\left[Q,\hat{C}_m,\lambda;0,h,0\right]=-\int_{X_w}^{\infty}\lambda^{(3)}(X,T_3)\,h^{(3)}(X,T_3)\,dX=0 \tag{3.59}$$

Applying Lemma 1 to equation (3.59) produces the necessary optimality condition,

$$\lambda^{(3)}(X,T_3)=0 \tag{3.60}$$

for all $X\in\left[X_w,\infty\right)$.

The necessary conditions for optimality to the first variation of ℓ with respect to λ are now applied. Suppose $\hat{\lambda}$ minimizes ℓ then necessarily $\delta\ell\left[Q, C_m, \hat{\lambda}; 0, 0, \mu\right] = 0$ for all admissible variations μ.

Case 1:

Choose μ such that

$$\mu(X,T) = 0 \quad \text{for all } X \in [X_w, \infty) \quad \text{and} \quad T \in [T_1, T_3]$$

then equation (3.23) becomes

$$\delta\ell\left[Q, C_m, \hat{\lambda}; 0, 0, \mu\right] = \int_0^{T_1}\int_{X_w}^{\infty} \mu^{(1)}(X,T)\begin{bmatrix} G\left[C_m^{(1)}\right](X,T) \\ +\beta\alpha^2 e^{-\alpha T}\int_0^T e^{\alpha\tau}\, C_m^{(1)}(X,\tau)\, d\tau \\ -\dfrac{\partial C_m^{(1)}(X,T)}{\partial T} \end{bmatrix} dXdT = 0 \tag{3.61}$$

Applying Lemma 2 to equation (3.61) produces the necessary optimality condition,

$$G\left[C_m^{(1)}\right](X,T) + \beta\alpha^2 e^{-\alpha T}\int_0^T e^{\alpha\tau}\, C_m^{(1)}(X,\tau)\, d\tau - \frac{\partial C_m^{(1)}(X,T)}{\partial T} = 0 \tag{3.62}$$

for all $X \in (X_w, \infty)$ and $T \in (0, T_1)$.

Case 2:

Choose μ such that

$$\mu(X,T) = 0 \quad \text{for all } X \in [X_w, \infty) \quad \text{and} \quad T \in [0, T_1] \cup [T_2, T_3]$$

then equation (3.23) becomes

$$\delta\ell\left[Q,C_m,\hat{\lambda};0,0,\mu\right]=\int_{T_1}^{T_2}\int_{X_w}^{\infty}\mu^{(2)}(X,T)\left[\begin{array}{l}G\left[C_m^{(2)}\right](X,T)\\+\beta\alpha^2e^{-\alpha T}\int_0^T e^{\alpha\tau}\,C_m^{(2)}(X,\tau)\,d\tau\\-\dfrac{\partial C_m^{(2)}(X,T)}{\partial T}\end{array}\right]dXdT=0 \tag{3.63}$$

Applying Lemma 2 to equation (3.63) produces the necessary optimality condition,

$$G\left[C_m^{(2)}\right](X,T)+\beta\alpha^2e^{-\alpha T}\int_0^T e^{\alpha\tau}\,C_m^{(2)}(X,\tau)\,d\tau-\frac{\partial C_m^{(2)}(X,T)}{\partial T}=0 \tag{3.64}$$

for all $X \in (X_w, \infty)$ and $T \in (T_1,T_2)$.

<u>Case 3:</u>

Choose μ such that

$$\mu(X,T)=0 \quad \text{for all } X\in[X_w,\infty) \quad \text{and} \quad T\in[0,T_2]$$

then equation (3.23) becomes

$$\delta\ell\left[Q,C_m,\hat{\lambda};0,0,\mu\right]=\int_{T_2}^{T_3}\int_{X_w}^{\infty}\mu^{(3)}(X,T)\left[\begin{array}{l}G\left[C_m^{(3)}\right](X,T)\\+\beta\alpha^2e^{-\alpha T}\int_0^T e^{\alpha\tau}\,C_m^{(3)}(X,\tau)\,d\tau\\-\dfrac{\partial C_m^{(3)}(X,T)}{\partial T}\end{array}\right]dXdT=0 \tag{3.65}$$

Applying Lemma 2 to equation (3.65) produces the necessary optimality condition,

$$G\left[C_m^{(3)}\right](X,T)+\beta\alpha^2e^{-\alpha T}\int_0^T e^{\alpha\tau}\,C_m^{(3)}(X,\tau)\,d\tau-\frac{\partial C_m^{(3)}(X,T)}{\partial T}=0 \tag{3.66}$$

for all $X \in (X_w, \infty)$ and $T \in (T_2,T_3)$.

We now have the necessary optimality conditions for all cases when applied to the first variation of $\mathcal{L}$ with respect to the functions $\hat{C}_m$ and $\hat{\lambda}$. Observe that if Q(T) is a given admissible pumping schedule and $\hat{C}_m(X,T)$ is a corresponding solution $\delta\mathcal{L}\left[Q,\hat{C}_m,\hat{\lambda};0,h,0\right]=0$ for all admissible variations h, then $\hat{\lambda}$ satisfies the following partial differential equations:

$$\begin{aligned}&\frac{\partial\hat{\lambda}}{\partial T}(X,T)+\frac{\partial^2}{\partial X^2}\left[\hat{\lambda}(X,T)\left(\frac{Q(T)}{X}+D\right)\right]-\frac{\partial}{\partial X}\left[\hat{\lambda}(X,T)\left(\frac{Q(T)}{X}+\frac{D}{X}\right)\right]\\&-\beta\alpha\hat{\lambda}(X,T)+\alpha^2\beta e^{\alpha T}\int_T^{T_{final}}e^{-\alpha t}\hat{\lambda}(X,t)\,dt=0\end{aligned} \tag{3.67}$$

for all $X\in(X_w,\infty)$ and for all $T\in(0,T_{final})$, and the following boundary conditions

$$\begin{aligned}&\frac{\partial f}{\partial C}\left[T,Q(T),\hat{C}_m(X_w,T)\right]\\&+\left\{\frac{\partial\hat{\lambda}}{\partial X}(X_w,T)\left(\frac{Q(T)}{X_w}+D\right)-\hat{\lambda}(X_w,T)\left(\frac{Q(T)}{X_w}+\frac{D}{X_w}\right)-\hat{\lambda}(X_w,T)\frac{Q(T)}{X_w^{\ 2}}\right\}=0\end{aligned} \tag{3.68}$$

for all $T\in[0,T_{final}]$ and

$$\hat{\lambda}(\infty,T)+\frac{\partial\hat{\lambda}}{\partial X}(\infty,T)=0 \tag{3.69}$$

for all $T\in[0,T_{final}]$. Also λ satisfies the terminal condition

$$\hat{\lambda}(X,T_{final})=0 \tag{3.70}$$

for all $X\in[X_w,\infty)$.

Additionally observe that if $\delta\mathcal{L}\left[Q,\hat{C}_m,\hat{\lambda};0,0,\mu\right]=0$ for all admissible variations μ then $\hat{C}_m$ satisfies the following partial differential equations:

$$G\left[\hat{C}_m\right](X,T)+\beta\alpha e^{-\alpha T}\,\hat{C}_{im,0}(X)+\beta\alpha^2 e^{-\alpha T}\int_0^T e^{\alpha\tau}\,\hat{C}_m(X,\tau)\,d\tau-\frac{\partial\hat{C}_m}{\partial T}=0 \qquad (3.71)$$

for all $X\in(X_w,\infty)$ and for all $T\in(0,T_{final})$.

Lastly notice that the variation of ℓ with respect to Q is modeled as the ordinary derivative with respect to T_1 and T_2. Observe if $\hat{T}_1$ and $\hat{T}_1$ yield a pumping schedule $\hat{Q}(T)$ which minimizes ℓ then $\frac{\partial\ell}{\partial T_1}\left[\hat{T}_1,\hat{T}_2,\hat{C}_m,\hat{\lambda}\right]=0$ and $\frac{\partial\ell}{\partial T_2}\left[\hat{T}_1,\hat{T}_2,\hat{C}_m,\hat{\lambda}\right]=0$ become

$$\begin{aligned}\frac{\partial\ell}{\partial T_1}&=f\left[\hat{T}_1,1,\hat{C}_m^{(1)}(X_w,\hat{T}_1)\right]-f\left[\hat{T}_1,0,\hat{C}_m^{(2)}(X_w,\hat{T}_1)\right]\\&-\hat{C}_m^{(1)}(X_w,\hat{T}_1)\frac{\partial f}{\partial C}\left[\hat{T}_1,1,\hat{C}_m^{(1)}(X_w,\hat{T}_1)\right]+\hat{C}_m^{(2)}(X_w,\hat{T}_1)\frac{\partial f}{\partial C}\left[\hat{T}_1,0,\hat{C}_m^{(2)}(X_w,\hat{T}_1)\right]=0\end{aligned} \qquad (3.72)$$

and

$$\begin{aligned}\frac{\partial\ell}{\partial T_2}&=f\left[\hat{T}_2,0,\hat{C}_m^{(2)}(X_w,\hat{T}_2)\right]-f\left[\hat{T}_2,1,\hat{C}_m^{(3)}(X_w,\hat{T}_2)\right]\\&-\hat{C}_m^{(2)}(X_w,\hat{T}_2)\frac{\partial f}{\partial C}\left[\hat{T}_2,0,\hat{C}_m^{(2)}(X_w,\hat{T}_2)\right]+\hat{C}_m^{(3)}(X_w,\hat{T}_2)\frac{\partial f}{\partial C}\left[\hat{T}_2,1,\hat{C}_m^{(3)}(X_w,\hat{T}_2)\right]=0\end{aligned} \qquad (3.73)$$

In order to solve for both $\frac{\partial\ell}{\partial T_1}$ and $\frac{\partial\ell}{\partial T_2}$ we must first solve for the concentration of the contaminant at the well, $C_m(X_w,T)$. This necessity motivates the need to solve the sorbing solute contaminant transport equation. Specifically, the partial differential equation for when the extraction well is on and off needs to be solved. Notice that equations (3.72) and (3.73) do not depend on λ, consequently there is no need to solve λ.

Governing Equations and Solutions

This section extends the theoretical development of the differential equations for sorbing solute contaminant transport and presents the governing equations and solutions for sorbing solute contaminant transport for conditions when an extraction well is turned on and when it is turned off. These equations follow the assumptions developed earlier in this chapter. A detailed mathematical analysis can be found in Appendix C (Well-on) and Appendix D (Well-off).

Model Formulation: Extraction Well On. The Laplace transform of equation (3.20), together with the appropriate boundary and initial conditions results in a single differential equation, including the assumption that molecular diffusion is negligible while mechanical dispersion dominates yields

$$\frac{1}{X}\frac{\partial^2 \overline{C}_m}{\partial X^2}+\frac{1}{X}\frac{\partial \overline{C}_m}{\partial X}-\gamma\,\overline{C}_m=\overline{F}(X,s) \tag{3.74}$$

where the overbar indicates the Laplace transformation of the function. Multiplying through by X results in

$$\frac{\partial^2 \overline{C}_m}{\partial X^2}+\frac{\partial \overline{C}_m}{\partial X}-X\gamma\,\overline{C}_m=X\overline{F}(X,s) \tag{3.75}$$

Assuming the solution of equation (3.74) has the following form

$$\overline{C}_m(X,s)=\phi(X,s)e^{-\frac{1}{2}x} \tag{3.76}$$

then substituting this equation into equation (3.75) yields

$$\frac{d^2\phi}{dx^2}-\gamma\left[X+\frac{1}{4\gamma}\right]\phi=e^{\frac{1}{2}x}\,X\overline{F}(X,s) \tag{3.77}$$

Employing the change of variables

$$y=\gamma^{\frac{1}{3}}\left[X+\frac{1}{4\gamma}\right],\quad X=\frac{y}{\gamma^{\frac{1}{3}}},\ \text{and}\ \Phi(y,s)=\phi(X,s)$$

leads to the following equation

$$\frac{d^2\Phi}{dy^2} - y\Phi = \gamma^{-\frac{2}{3}} e^{\left(\frac{1}{2}\left[\frac{y}{\gamma^{\frac{1}{3}}} - \frac{1}{4\gamma}\right]\right)} \overline{F}\left(\frac{y}{\gamma^{\frac{1}{3}}} - \frac{1}{4\gamma}, s\right) \qquad y_w < y < \infty \tag{3.78}$$

see (Adams & Viramontes, 1993) pages A-64 through A-65 for derivation and rationale for variable change. Subject to the following boundary conditions, again see (Adams & Viramontes, 1993) pages A-65 through A-68 for rationale and derivation.

$$-\frac{1}{2}\Phi(y_w) + \gamma^{\frac{1}{3}}\frac{d\Phi(y_w)}{dy} = 0 \tag{3.79}$$

$$\frac{1}{2}\Phi(\infty) + \gamma^{\frac{1}{3}}\frac{d\Phi(\infty)}{dy} = 0 \tag{3.80}$$

Equation (3.78) has the solution in the form

$$\Phi(y,s) = \int_{y_w}^{\infty} g(y,\eta,s)\mathcal{F}(\eta,s)\,d\eta \tag{3.81}$$

where $g(y,\eta,s)$ is the Green's function given by:

$$g(y,\eta,s) = \begin{cases} \dfrac{\Phi_1(y)\Phi_2(\eta)}{W[\Phi_1,\Phi_2](\eta)} & y < \eta < \infty \\ \dfrac{\Phi_1(\eta)\Phi_2(y)}{W[\Phi_1,\Phi_2](\eta)} & y_w \le \eta \le y \end{cases} \tag{3.82}$$

where $W[\Phi_1,\Phi_2](\eta)$ is the Wronskian of Φ_1 and Φ_2, and Φ_1 satisfies equations (3.78) and (3.79) and Φ_2 satisfies equations (3.78) and (3.80).

To find the solution to $\Phi_1(y)$ we apply the boundary condition at y_w, which is equation (3.79). Solving for Φ_1 and applying the boundary conditions at y_w yields:

$$\Phi_1(y) = A\left[Ai(y) - \frac{G[Ai]}{G[Bi]}Bi(y)\right] \tag{3.83}$$

where

$$G[Ai] = -\frac{1}{2}Ai(y_w) + \gamma^{\frac{1}{3}}\frac{dAi}{dy}(y_w) \tag{3.84}$$

and

$$G[Bi] = -\frac{1}{2}Bi(y_w) + \gamma^{\frac{1}{3}}\frac{dBi}{dy}(y_w) \tag{3.85}$$

where Ai(y) and Bi(y) are Airy and Bairy functions, respectively (Abramowitz and Stegun, 1970).

To find the solution $\Phi_2(y)$, we apply the boundary conditions at $y = \infty$ which yields:

$$\Phi_2(y) = CAi(y) \tag{3.86}$$

and the value of the Wronskian becomes

$$W[\Phi_1, \Phi_2](y) = AC\left[\frac{G[Ai]}{G[Bi]}\right]\frac{1}{\pi} \tag{3.87}$$

Substituting into equation (3.82) the Green's function yields

$$g(y,\eta)=\begin{cases}\dfrac{A\left[Ai(y)-\dfrac{G[Ai]}{G[Bi]}Bi(y)\right]CAi(\eta)}{AC\left[\dfrac{G[Ai]}{G[Bi]}\right]\dfrac{1}{\pi}} & y<\eta<\infty\\[2ex] \dfrac{A\left[Ai(\eta)-\dfrac{G[Ai]}{G[Bi]}Bi(\eta)\right]CAi(y)}{AC\left[\dfrac{G[Ai]}{G[Bi]}\right]\dfrac{1}{\pi}} & y_w\le\eta\le y\end{cases} \tag{3.88}$$

Simplifying the Green's function bec...

$$\pi\left[Ai(y)\frac{G[Bi]}{G[Ai]}-Bi(y)\right]Ai(\eta) \qquad y<\eta<\infty \tag{3.89}$$

and

$$\pi\left[Ai(\eta)\frac{G[Bi]}{G[Ai]}-Bi(\eta)\right]Ai(y) \qquad y_w\le\eta\le y \tag{3.90}$$

Through a manipulation of variables $\overline{C}_m(X,s)$ becomes,

$$\overline{C}_m(X,s)=e^{-\frac{1}{2}x}\int_{x_w}^{\infty}b(x,\xi,s)\gamma^{-\frac{1}{3}}e^{\frac{1}{2}\xi}\,\overline{F}(\xi,s)\,d\xi \tag{3.91}$$

see (Adams & Viramontes, 1993, pages A-77 through A-78) for a more thorough derivation and explanation. The nonhomogeneous boundary-value problem has the unique solution

$$\begin{aligned}\Phi(y)&=\pi\frac{G[Bi]}{G[Ai]}Ai(y)\int_{y_w}^{y}Ai(\eta)\mathcal{F}(\eta,s)\,d\eta-\pi Ai(y)\int_{y_w}^{y}Bi(\eta)\mathcal{F}(\eta,s)\,d\eta\\&+\pi\frac{G[Bi]}{G[Ai]}Ai(y)\int_{y}^{\infty}Ai(\eta)\mathcal{F}(\eta,s)\,d\eta-\pi Bi(y)\int_{y}^{\infty}Ai(\eta)\mathcal{F}(\eta,s)\,d\eta\end{aligned} \tag{3.92}$$

Combining equation (3.91) and (3.92) results in the solution

$$\overline{C}_m(X,s) = \pi e^{-\frac{1}{2}X}\gamma^{-\frac{1}{3}}\left\{\begin{array}{l} \frac{G[Bi]}{G[Ai]}Ai\left[\gamma^{\frac{1}{3}}\left(X+\frac{1}{4\gamma}\right)\right]\int_{X_w}^{X} Ai\left[\gamma^{\frac{1}{3}}\left(\xi+\frac{1}{4\gamma}\right)\right]e^{\frac{1}{2}\xi}\,\overline{F}(\xi,s)\,d\xi \\ -Ai\left[\gamma^{\frac{1}{3}}\left(X+\frac{1}{4\gamma}\right)\right]\int_{X_w}^{X} Bi\left[\gamma^{\frac{1}{3}}\left(\xi+\frac{1}{4\gamma}\right)\right]e^{\frac{1}{2}\xi}\,\overline{F}(\xi,s)\,d\xi \\ +\frac{G[Bi]}{G[Ai]}Ai\left[\gamma^{\frac{1}{3}}\left(X+\frac{1}{4\gamma}\right)\right]\int_{X}^{\infty} Ai\left[\gamma^{\frac{1}{3}}\left(\xi+\frac{1}{4\gamma}\right)\right]e^{\frac{1}{2}\xi}\,\overline{F}(\xi,s)\,d\xi \\ -Bi\left[\gamma^{\frac{1}{3}}\left(X+\frac{1}{4\gamma}\right)\right]\int_{X}^{\infty} Ai\left[\gamma^{\frac{1}{3}}\left(\xi+\frac{1}{4\gamma}\right)\right]e^{\frac{1}{2}\xi}\,\overline{F}(\xi,s)\,d\xi \end{array}\right\}$$

(3.93)

Solving for $\overline{C}_m(X_w,s)$ at the well results in the following equation where the first and second term in equation (3.93) are zero at the well.

$$\overline{C}_m(X_w,s) = \pi e^{-\frac{1}{2}X}\gamma^{-\frac{1}{3}}\left[\frac{G[Bi]}{G[Ai]}Ai(y_w) - Bi(y_w)\right]\int_{X_w}^{\infty} Ai\left[\gamma^{\frac{1}{3}}\left(\xi+\frac{1}{4\gamma}\right)\right]e^{\frac{1}{2}\xi}\,\overline{F}(\xi,s)\,d\xi \qquad (3.94)$$

which yields the following solution to $\overline{C}_m(X_w,s)$ in the Laplace domain:

$$\overline{C}_m(X_w,s) = \frac{e^{-\frac{1}{2}X}}{G[Ai]}\int_{X_w}^{\infty} Ai\left[\gamma^{\frac{1}{3}}\left(\xi+\frac{1}{4\gamma}\right)\right]e^{\frac{1}{2}\xi}\,\overline{F}(\xi,s)\,d\xi \qquad (3.95)$$

Model Formulation: Extraction Well Off. The Laplace transform equation (3.20), together with the appropriate boundary and initial conditions results in a single differential equation, including the assumption that mechanical dispersion is negligible while molecular diffusion dominates yields

$$D\frac{\partial^2 \overline{C}_m}{\partial X^2}+\frac{D}{X}\frac{\partial \overline{C}_m}{\partial X}-\gamma\,\overline{C}_m=\overline{F}(X,s) \tag{3.96}$$

where the overbar indicates the Laplace Transform of the corresponding functions. Multiplying through by X/D and defining the

$$\Im(X,s)=D^{-1}\overline{F}(X,s) \tag{3.97}$$

and

$$\tilde{\gamma}=D^{-1}\gamma \tag{3.98}$$

results in the differential equation

$$X\frac{\partial^2 \overline{C}_m}{\partial X^2}+\frac{\partial \overline{C}_m}{\partial X}-X\tilde{\gamma}\,\overline{C}_m=X\Im(X,s) \tag{3.99}$$

Assume the solution to the differential equation (3.96) has the form

$$\overline{C}_m(X,s)=\phi(X,s) \tag{3.100}$$

Substituting into equation (3.99) yields:

$$X\frac{d^2\phi(X,s)}{dX^2}+\frac{d\phi(X,s)}{dX}-\tilde{\gamma}\,X\phi(X,s)=X\Im(X,s) \tag{3.101}$$

Defining the new independent variable

$$y=\tilde{\gamma}^{\frac{1}{2}}X \tag{3.102}$$

and the new dependent variable

$$\Phi(y,s)=\phi(X,s) \tag{3.103}$$

and dividing equation (3.101) by y^2 becomes

$$\frac{d^2\Phi(y,s)}{dy^2}+\frac{1}{y}\frac{d\Phi(y,s)}{dy}-\Phi(y,s)=\frac{1}{\tilde{\gamma}}\mathfrak{F}(\frac{y}{\tilde{\gamma}^{\frac{1}{2}}},s)\equiv\mathfrak{F}^{*}(y,s) \tag{3.104}$$

on the interval $y_w < y < \infty$.

Looking at the Laplace transformed boundary condition at the dimensionless well radius (see Equation D.5, Appendix D) and converting it into terms of y_w yields:

$$\frac{d\Phi}{dy}(y_w,s)=0 \tag{3.105}$$

where

$$y_w=\tilde{\gamma}^{\frac{1}{2}}X_w \tag{3.106}$$

The boundary condition at infinity can be rewritten in terms of $y = \infty$ as

$$\tilde{\gamma}^{\frac{1}{2}}\frac{d\Phi}{dy}(\infty,s)+\Phi(\infty,s)=0 \tag{3.107}$$

since

$$y=\tilde{\gamma}^{\frac{1}{2}}X \tag{3.108}$$

then as $X \to \infty$, we have that $y \to \infty$.

To find the first solution, $\Phi_1(y,s)$, we apply the boundary condition at the well (equation 3.106) which yields

$$\Phi_1(y,s)=-K_o'(y_w)I_o(y)+I_o'(y_w)K_o(y) \tag{3.109}$$

where $I_o(y)$ and $K_o(y)$ are Bessel functions of the first kind, order zero and third kind, order zero, respectively.

To find the solution, $\Phi_2(y,s)$ we apply the boundary condition at y = ∞ (equation 3.104) which yields

$$\Phi_2(y,s) = DK_o(y) \tag{3.110}$$

We now seek the particular solution to equation (3.101) using a Green's function which is of the form:

$$g(y,\eta,s) = \begin{cases} \dfrac{\Phi_1(y)\Phi_2(\eta)}{W[\Phi_1,\Phi_2](\eta)} & y < \eta < \infty \\ \dfrac{\Phi_1(\eta)\Phi_2(y)}{W[\Phi_1,\Phi_2](\eta)} & y_w \le \eta \le y \end{cases} \tag{3.111}$$

The Wronskian of Φ_1 and Φ_2 is denoted by $W[\Phi_1,\Phi_2](\eta)$ and is determined to be

$$W[\Phi_1,\Phi_2](y) = \frac{1}{y}K_o'(y_w) \tag{3.112}$$

Thus the Green's function becomes

$$g(y,\eta,s) = \begin{cases} \dfrac{\eta[I_o'(y_w)K_o(y) - K_o'(y_w)I_o(y)]K_o(\eta)}{K_o'(y_w)} & y < \eta < \infty \\ \dfrac{\eta[I_o'(y_w)K_o(\eta) - K_o'(y_w)I_o(\eta)]K_o(y)}{K_o'(y_w)} & y_w \le \eta \le y \end{cases}$$

(3.113)

The general solution to equation (3.104) is of the form

$$\Phi(y) = \int_{y_w}^{\infty} g(y,\eta,s)\mathcal{F}^*(\eta,s)\,d\eta \tag{3.114}$$

Since $y = \tilde{\gamma}^{\frac{1}{2}} X$, then $\eta = \tilde{\gamma}^{\frac{1}{2}}\xi$ and $d\eta = \tilde{\gamma}^{\frac{1}{2}} d\xi$. Thus equation (3.114), together with the right hand side of equation (3.104) becomes

$$\Phi(y,s) = \int_{X_w}^{\infty} g\left(\tilde{\gamma}^{\frac{1}{2}} X, \tilde{\gamma}^{\frac{1}{2}}\xi, s\right) \mathcal{J}^{*}\left(\tilde{\gamma}^{\frac{1}{2}}\xi, s\right) \tilde{\gamma}^{\frac{1}{2}} d\xi \tag{3.115}$$

$$= \int_{X_w}^{\infty} g\left(\tilde{\gamma}^{\frac{1}{2}} X, \tilde{\gamma}^{\frac{1}{2}}\xi, s\right) \tilde{\gamma}^{-\frac{1}{2}} \overline{F}(\xi, s) \tilde{\gamma}^{\frac{1}{2}} d\xi \tag{3.116}$$

Since $\overline{C}_m(X,s) = \phi(X,s)$ and $\Phi(y,s) = \phi(X,s)$ then

$$\overline{C}_m(X,s) = \int_{X_w}^{\infty} g\left(\tilde{\gamma}^{\frac{1}{2}} X, \tilde{\gamma}^{\frac{1}{2}}\xi, s\right) \overline{F}(\xi, s) d\xi \tag{3.117}$$

If we define

$$\mathcal{G}(X, \xi, s) = g\left(\tilde{\gamma}^{\frac{1}{2}} X, \tilde{\gamma}^{\frac{1}{2}}\xi, s\right) \tag{3.118}$$

then

$$\overline{C}_m(X,s) = \int_{X_w}^{\infty} \mathcal{G}(X, \xi, s) \overline{F}(\xi, s) d\xi \tag{3.119}$$

Substituting in the constructed Green's functions (equation 3.113) using equation (3.104) yields

$$\begin{aligned} \Phi(y) = {} & \frac{I_o'(y_w)}{K_o'(y_w)} K_o(y) \int_{y_w}^{y} \eta K_o(\eta) \mathcal{J}^{*}(\eta, s) d\eta - K_o(y) \int_{y_w}^{y} \eta I_o(\eta) \mathcal{J}^{*}(\eta, s) d\eta \\ & + \frac{I_o'(y_w)}{K_o'(y_w)} K_o(y) \int_{y}^{\infty} \eta K_o(\eta) \mathcal{J}^{*}(\eta, s) d\eta - I_o(y) \int_{y}^{\infty} \eta K_o(\eta) \mathcal{J}^{*}(\eta, s) d\eta \end{aligned} \tag{3.120}$$

Therefore,

$$\overline{C}_m(X,s) = \begin{bmatrix} \dfrac{I_o'(y_w)}{K_o'(y_w)} K_o\left(\tilde{\gamma}^{\frac{1}{2}} X\right) \int_{X_w}^{\infty} \xi K_o\left(\tilde{\gamma}^{\frac{1}{2}} \xi\right) \overline{F}(\xi,s)\, d\xi \\ -K_o\left(\tilde{\gamma}^{\frac{1}{2}} X\right) \int_{X_w}^{X} \xi I_o\left(\tilde{\gamma}^{\frac{1}{2}} \xi\right) \overline{F}(\xi,s)\, d\xi \\ -I_o\left(\tilde{\gamma}^{\frac{1}{2}} X\right) \int_{X_w}^{\infty} \xi K_o\left(\tilde{\gamma}^{\frac{1}{2}} \xi\right) \overline{F}(\xi,s)\, d\xi \end{bmatrix} \tag{3.121}$$

Solving for $\overline{C}_m(X_w,s)$ at the well results in the following equation where the second term in equation (3.120) is zero at the well which yields the following solution to $\overline{C}_m(X_w,s)$ in the Laplace domain:

$$\overline{C}_m(X_w,s) = \frac{\tilde{\gamma}^{\frac{1}{2}}}{X_w K_o'\left(\tilde{\gamma}^{\frac{1}{2}} X_w\right)} \int_{X_w}^{\infty} \xi K_o\left(\tilde{\gamma}^{\frac{1}{2}} \xi\right) \overline{F}(\xi,s)\, d\xi \tag{3.122}$$

To determine the concentration at the well in the time domain we need to perform an inverse Laplace Transform of $\overline{C}_m(X_w,s)$ in (3.122). That is,

$$C_m(X_w,T) = \mathcal{L}^{1}\left[\frac{\tilde{\gamma}^{\frac{1}{2}}}{X_w K_o'\left(\tilde{\gamma}^{\frac{1}{2}} X_w\right)} \int_{X_w}^{\infty} \xi K_o\left(\tilde{\gamma}^{\frac{1}{2}} \xi\right) \overline{F}(\xi,s)\, d\xi\right] \tag{3.123}$$

Necessary Optimality Conditions for the Second Variation

Utilizing the procedure to determine the necessary optimality conditions for the first variation of $\mathcal{L}$ shows that we have a candidate for an optimal solution, however, it does not state whether or not the optimal solution is a maximum, minimum or neither. To address this issue the concept of the second variation will be introduced and utilized.

The concept of the second variation expands the first variation, where the second variation is generally denoted as $\delta^2 J[y;h]$, where the functional $J[y]$ is assumed to be twice differentiable at $\hat{y}$ along the increment h (Gelfand & Fomin, 1963:99).

Second Variation. With the first variation determined for the Lagrangian with respect to each variable, C_m, λ, and Q, the second variation can be determined in order to determine the necessary optimality conditions for the second variation, which is defined by the following theorem:

> Theorem 1. *A necessary condition for the functional* $J[y]$ *to have a minimum for* $y = \hat{y}$ *is that* $\delta^2 J[\hat{y};h] \geq 0$ *for* $y = \hat{y}$ *and all admissible variations* h. *For a maximum,* $\delta^2 J[\hat{y};h] \leq 0$ (Gelfand & Fomin, 1963:99).

Referencing the first variation of $\mathcal{L}$ with respect to λ in the direction of μ (see equation 3.30), it is easy to determine the second variation of $\mathcal{L}$ with respect to λ in the direction of μ which is,

$$\delta^2 \mathcal{L}[Q, C_m\, \lambda; 0, 0, \mu] = \lim_{a \to 0} \frac{1}{2} \frac{d^2}{da^2} \mathcal{L}[Q, C_m, \lambda + a\,\mu] = 0 \tag{3.124}$$

Additionally, utilizing the first variation of $\mathcal{L}$ with respect to C_m in the direction of h, equation (3.30), it is easy to determine the second variation of $\mathcal{L}$ with respect to C_m in the direction of h as,

$$\delta^2 \mathcal{L}[Q, C_m, \lambda; 0, h\, 0] = \lim_{a \to 0} \frac{1}{2} \frac{d^2}{da^2} \mathcal{L}[Q, C + ah, \lambda] = \int_0^{T_{final}} \frac{\partial^2 f}{\partial C^2}[T, Q(T), C_m(X_w, T)]\, h^2(X_w, T)\, dT \tag{3.125}$$

Unlike the previous derivations the second variation of $\mathcal{L}$ with respect to Q is more complicated and can be evaluated by examining the variation of $\mathcal{L}$ with respect to T_1 and T_2. First the variation of $\mathcal{L}$ with respect to T_1 is accomplished by first referencing equation (3.39). In fact, this is just the second derivative of $\mathcal{L}$ with respect to T_1.

$$
\begin{aligned}
\frac{\partial^2}{\partial T_1^2}\mathcal{L} &= \frac{\partial f}{\partial T}\left[T_1, 1, C_m^{(1)}(X_w, T_1)\right] + \frac{\partial f}{\partial C}\left[T_1, 1, C_m^{(1)}(X_w, T_1)\right]\frac{\partial C_m^{(1)}}{\partial T}(X_w, T_1) \\
&- \frac{\partial f}{\partial T}\left[T_1, 0, C_m^{(2)}(X_w, T_1)\right] - \frac{\partial f}{\partial C}\left[T_1, 0, C_m^{(2)}(X_w, T_1)\right]\frac{\partial C_m^{(2)}}{\partial T}(X_w, T_1) \\
&+ \int_{X_w}^{\infty} \frac{\partial C_m^{(1)}}{\partial T}(X, T_1)\left\{\begin{array}{l} \frac{\partial \lambda^{(1)}}{\partial T}(X, T_1) + \frac{\partial^2}{\partial X^2}\left[\lambda^{(1)}(X, T_1)\left(\frac{1}{X} + D\right)\right] - \frac{\partial}{\partial X}\left[\lambda^{(1)}(X, T_1)\left(\frac{1}{X} + \frac{D}{X}\right)\right] \\ -\beta\alpha\lambda^{(1)}(X, T_1) + \alpha^2\beta e^{\alpha T_1}\left[\int_{T_1}^{T_2} e^{-\alpha t}\lambda^{(2)}(X, t)\,dt + \int_{T_2}^{T_3} e^{-\alpha t}\lambda^{(3)}(X, t)\,dt\right] \end{array}\right\} dX \\
&+ \int_{X_w}^{\infty} C_m^{(1)}(X, T_1)\left\{\begin{array}{l} \frac{\partial^2 \lambda^{(1)}}{\partial T^2}(X, T_1) + \frac{\partial^2}{\partial X^2}\left[\frac{\partial \lambda^{(1)}}{\partial T}(X, T_1)\left(\frac{1}{X} + D\right)\right] - \frac{\partial}{\partial X}\left[\frac{\partial \lambda^{(1)}}{\partial T}(X, T_1)\left(\frac{1}{X} + \frac{D}{X}\right)\right] \\ -\beta\alpha\frac{\partial \lambda^{(1)}}{\partial T}(X, T_1) + \alpha^3\beta e^{\alpha T_1}\left[\int_{T_1}^{T_2} e^{-\alpha t}\lambda^{(2)}(X, t)\,dt + \int_{T_2}^{T_3} e^{-\alpha t}\lambda^{(3)}(X, t)\,dt\right] \\ -\alpha^2\beta e^{\alpha T_1}\left[e^{-\alpha T_1}\lambda^{(2)}(X, T_1)\right] \end{array}\right\} dX \\
&- \int_{X_w}^{\infty} \frac{\partial C_m^{(2)}}{\partial T}(X, T_1)\left\{\begin{array}{l} \frac{\partial \lambda^{(2)}}{\partial T}(X, T_1) + \frac{\partial^2}{\partial X^2}\left[\lambda^{(2)}(X, T_1)D\right] - \frac{\partial}{\partial X}\left[\lambda^{(2)}(X, T_1)\left(\frac{D}{X}\right)\right] \\ -\beta\alpha\lambda^{(2)}(X, T_1) + \alpha^2\beta e^{\alpha T_1}\left[\int_{T_1}^{T_2} e^{-\alpha t}\lambda^{(2)}(X, t)\,dt + \int_{T_2}^{T_3} e^{-\alpha t}\lambda^{(3)}(X, t)\,dt\right] \end{array}\right\} dX \\
&- \int_{X_w}^{\infty} C_m^{(2)}(X, T_1)\left\{\begin{array}{l} \frac{\partial^2 \lambda^{(2)}}{\partial T^2}(X, T_1) + \frac{\partial^2}{\partial X^2}\frac{\partial \lambda^{(2)}}{\partial T}(X, T_1)D - \frac{\partial}{\partial X}\left[\frac{\partial \lambda^{(2)}}{\partial T}(X, T_1)\frac{D}{X}\right] \\ -\beta\alpha\frac{\partial \lambda^{(2)}}{\partial T}(X, T_1) + \alpha^3\beta e^{\alpha T_1}\left[\int_{T_1}^{T_2} e^{-\alpha t}\lambda^{(2)}(X, t)\,dt + \int_{T_2}^{T_3} e^{-\alpha t}\lambda^{(3)}(X, t)\,dt\right] \\ +\alpha^2\beta e^{\alpha T_1}\left[e^{-\alpha T_1}\lambda^{(2)}(X, T_1)\right] \end{array}\right\} dX \\
&- D\frac{\partial C_m^{(1)}}{\partial T}(\infty, T_1)\left[\lambda^{(1)}(\infty, T_1) + \frac{\partial \lambda^{(1)}}{\partial X}(\infty, T_1)\right] - DC_m^{(1)}(\infty, T_1)\left[\frac{\partial \lambda^{(1)}}{\partial T}(\infty, T_1) + \frac{\partial}{\partial X}\frac{\partial \lambda^{(1)}}{\partial T}(\infty, T_1)\right]
\end{aligned}
$$

$$+D\frac{\partial C_m^{(2)}}{\partial T}(\infty,T_1)\left[\lambda^{(2)}(\infty,T_1)+\frac{\partial\lambda^{(2)}}{\partial X}(\infty,T_1)\right]+DC_m^{(2)}(\infty,T_1)\left[\frac{\partial\lambda^{(2)}}{\partial T}(\infty,T_1)+\frac{\partial}{\partial X}\frac{\partial\lambda^{(2)}}{\partial T}(\infty,T_1)\right]$$
$$+\frac{\partial C_m^{(1)}}{\partial T}(X_w,T_1)\left\{\frac{\partial\lambda^{(1)}}{\partial X}(X_w,T_1)\left(\frac{1}{X_w}+D\right)-\lambda^{(1)}(X_w,T_1)\left(\frac{1}{X_w}+\frac{D}{X_w}\right)-\lambda^{(1)}(X_w,T_1)\frac{1}{X_w{}^2}\right\}$$
$$+C_m^{(1)}(X_w,T_1)\left\{\frac{\partial}{\partial X}\frac{\partial\lambda^{(1)}}{\partial T}(X_w,T_1)\left(\frac{1}{X_w}+D\right)-\frac{\partial\lambda^{(1)}}{\partial T}(X_w,T_1)\left(\frac{1}{X_w}+\frac{D}{X_w}\right)-\frac{\partial\lambda^{(1)}}{\partial T}(X_w,T_1)\frac{1}{X_w{}^2}\right\}$$
$$-\frac{\partial C_m^{(2)}}{\partial T}(X_w,T_1)\left\{\frac{\partial\lambda^{(2)}}{\partial X}(X_w,T_1)D-\lambda^{(2)}(X_w,T_1)\frac{D}{X_w}\right\}$$
$$-C_m^{(2)}(X_w,T_1)\left\{\frac{\partial}{\partial X}\frac{\partial\lambda^{(2)}}{\partial T}(X_w,T_1)D-\frac{\partial\lambda^{(2)}}{\partial T}(X_w,T_1)\frac{D}{X_w}\right\} \tag{3.126}$$

Similarly the second derivative of ℓ with respect to T_2 is,

$$\frac{\partial^2}{\partial T_2{}^2}\ell=\frac{\partial f}{\partial T}\left[T_2,0,C_m^{(2)}(X_w,T_2)\right]+\frac{\partial f}{\partial C}\left[T_2,0,C_m^{(2)}(X_w,T_2)\right]\frac{\partial C_m^{(2)}}{\partial T}(X_w,T_2)$$
$$-\frac{\partial f}{\partial T}\left[T_2,1,C_m^{(3)}(X_w,T_2)\right]-\frac{\partial f}{\partial C}\left[T_2,1,C_m^{(3)}(X_w,T_2)\right]\frac{\partial C_m^{(3)}}{\partial T}(X_w,T_2)$$
$$+\int_{X_w}^{\infty}\frac{\partial C_m^{(2)}}{\partial T}(X,T_2)\left\{\begin{array}{l}\frac{\partial\lambda^{(2)}}{\partial T}(X,T_2)+\frac{\partial^2}{\partial X^2}\left[\lambda^{(2)}(X,T_2)(D)\right]-\frac{\partial}{\partial X}\left[\lambda^{(2)}(X,T_2)\left(\frac{D}{X}\right)\right]\\ -\beta\alpha\lambda^{(2)}(X,T_2)+\alpha^2\beta e^{\alpha T_2}\int_{T_2}^{T_3}e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\end{array}\right\}dX$$
$$+\int_{X_w}^{\infty}C_m^{(2)}(X,T_2)\left\{\begin{array}{l}\frac{\partial^2\lambda^{(2)}}{\partial T^2}(X,T_2)+\frac{\partial^2}{\partial X^2}\frac{\partial\lambda^{(2)}}{\partial T}(X,T_2)D-\frac{\partial}{\partial X}\left[\frac{\partial\lambda^{(2)}}{\partial T}(X,T_2)\frac{D}{X}\right]\\ -\beta\alpha\frac{\partial\lambda^{(2)}}{\partial T}(X,T_2)+\alpha^3\beta e^{\alpha T_2}\int_{T_2}^{T_3}e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\\ -\alpha^2\beta e^{\alpha T_2}\left(e^{-\alpha T_2}\lambda^{(3)}(X,T_2)\right)\end{array}\right\}dX$$
$$-\int_{X_w}^{\infty}\frac{\partial C_m^{(3)}}{\partial T}(X,T_2)\left\{\begin{array}{l}\frac{\partial\lambda^{(3)}}{\partial T}(X,T_2)+\frac{\partial^2}{\partial X^2}\left[\lambda^{(3)}(X,T_2)\left(\frac{1}{X}+D\right)\right]-\frac{\partial}{\partial X}\left[\lambda^{(3)}(X,T_2)\left(\frac{1}{X}+\frac{D}{X}\right)\right]\\ -\beta\alpha\lambda^{(3)}(X,T_2)+\alpha^2\beta e^{\alpha T_2}\int_{T_2}^{T_3}e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\end{array}\right\}dX$$
$$-\int_{X_w}^{\infty}C_m^{(3)}(X,T_2)\left\{\begin{array}{l}\frac{\partial^2\lambda^{(3)}}{\partial T^2}(X,T_2)+\frac{\partial^2}{\partial X^2}\left[\frac{\partial\lambda^{(3)}}{\partial T}(X,T_2)\left(\frac{1}{X}+D\right)\right]-\frac{\partial}{\partial X}\left[\frac{\partial\lambda^{(3)}}{\partial T}(X,T_2)\left(\frac{1}{X}+\frac{D}{X}\right)\right]\\ -\beta\alpha\frac{\partial\lambda^{(3)}}{\partial T}(X,T_2)+\alpha^3\beta e^{\alpha T_2}\left(\int_{T_2}^{T_3}e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\right)+\alpha^2\beta e^{\alpha T_2}\left(e^{-\alpha T_2}\lambda^{(3)}(X,T_2)\right)\end{array}\right\}dX$$

$$-D\frac{\partial C_m^{(2)}}{\partial T}(\infty,T_2)\left[\lambda^{(2)}(\infty,T_2)+\frac{\partial\lambda^{(2)}}{\partial X}(\infty,T_2)\right]-DC_m^{(2)}(\infty,T_2)\left[\frac{\partial\lambda^{(2)}}{\partial T}(\infty,T_2)+\frac{\partial}{\partial X}\frac{\partial\lambda^{(2)}}{\partial T}(\infty,T_2)\right]$$

$$+D\frac{\partial C_m^{(3)}}{\partial T}(\infty,T_2)\left[\lambda^{(3)}(\infty,T_2)+\frac{\partial\lambda^{(3)}}{\partial X}(\infty,T_2)\right]+DC_m^{(3)}(\infty,T_2)\left[\frac{\partial\lambda^{(3)}}{\partial T}(\infty,T_2)+\frac{\partial}{\partial X}\frac{\partial\lambda^{(3)}}{\partial T}(\infty,T_2)\right]$$

$$+\frac{\partial C_m^{(2)}}{\partial T}(X_w,T_2)\left\{\frac{\partial\lambda^{(2)}}{\partial X}(X_w,T_2)D-\lambda^{(2)}(X_w,T_2)\frac{D}{X_w}\right\}$$

$$+C_m^{(2)}(X_w,T_2)\left\{\frac{\partial}{\partial X}\frac{\partial\lambda^{(2)}}{\partial T}(X_w,T_2)D-\frac{\partial\lambda^{(2)}}{\partial T}(X_w,T_2)\frac{D}{X_w}\right\}$$

$$-\frac{\partial C_m^{(3)}}{\partial T}(X_w,T_2)\left\{\frac{\partial\lambda^{(3)}}{\partial X}(X_w,T_2)\left(\frac{1}{X_w}+D\right)-\lambda^{(3)}(X_w,T_2)\left(\frac{1}{X_w}+\frac{D}{X_w}\right)-\lambda^{(3)}(X_w,T_2)\frac{1}{X_w^{\,2}}\right\}$$

$$-C_m^{(3)}(X_w,T_2)\left\{\frac{\partial}{\partial X}\frac{\partial\lambda^{(3)}}{\partial T}(X_w,T_2)\left(\frac{1}{X_w}+D\right)-\frac{\partial\lambda^{(3)}}{\partial T}(X_w,T_2)\left(\frac{1}{X_w}+\frac{D}{X_w}\right)-\frac{\partial\lambda^{(3)}}{\partial T}(X_w,T_2)\frac{1}{X_w^{\,2}}\right\}$$

(3.127)

Application of the Necessary Optimality Condition for the Second Variation. Utilizing the second variations we can determine the necessary optimality conditions for the second variation of $\mathcal{L}$. For the functionals considered this thesis, the second variation yields a quadratic functional, hence the following lemma will be of use.

Lemma 3. *If* A(T) *is continuous on* [a,b] *and if*

$$\int_a^b A(T)\,h^2(T)\,dT \ge 0$$

for every function h which is continuous on [a,b] *such that* h(a) = h(b) =0, *then* $A(T) \ge 0$ *for all* $T \in [a,b]$.

The necessary conditions for optimality to the second variation of $\mathcal{L}$ with respect to C_m are applied now. Suppose $\hat{C}_m$ minimizes $\mathcal{L}$ then $\delta^2\mathcal{L}\left[Q,\hat{C}\,\lambda;0,h,0\right]=0$ for all admissible variations h.

Case 1:

Choose h such that

$$h(X,T) = 0 \text{ for all } T \in [T_1, T_3] \text{ and } X \in [X_w, \infty)$$

such that

$$h(X_w, T) \neq 0 \text{ for some } T \in [0, T_1)$$

then equation (3.125) becomes

$$\delta^2 \ell[Q, \hat{C}_m, \lambda; 0, h, 0] = \int_0^{T_1} \frac{\partial^2 f}{\partial C^2}\left[T, Q(T), \hat{C}_m^{(1)}(X_w, T)\right]\left[h^{(1)}(X_w, T)\right]^2 dT \geq 0 \tag{3.128}$$

Applying Lemma 3 to equation (3.128) is a necessary optimality condition,

$$\frac{\partial^2 f}{\partial C^2}\left[T, Q(T), \hat{C}_m^{(1)}(X_w, T)\right] \geq 0 \tag{3.129}$$

for all $T \in [0, T_1]$.

Case 2:

Choose h such that

$$h(X,T) = 0 \text{ for all } T \in [0, T_1] \cup [T_2, T_3] \text{ and } X \in [X_w, \infty)$$

and

$$h(X_w, T) \neq 0 \text{ for some } T \in (T_1, T_2)$$

then equation (3.125) becomes

$$\delta^2 \ell[Q, \hat{C}_m, \lambda; 0, h, 0] = \int_{T_1}^{T_2} \frac{\partial^2 f}{\partial C^2}\left[T, Q(T), \hat{C}_m^{(2)}(X_w, T)\right]\left[h^{(2)}(X_w, T)\right]^2 dT \geq 0 \tag{3.130}$$

Applying Lemma 3 to equation (3.130) produces the necessary optimality condition,

$$\frac{\partial^2 f}{\partial C^2}\left[T, Q(T), \hat{C}_m^{(2)}(X_w, T)\right] \geq 0 \tag{3.131}$$

for all $T \in [T_1, T_2]$.

Case 3:

Choose h such that

$$h(X,T) = 0 \text{ for all } T \in [0, T_2] \text{ and } X \in [X_w, \infty)$$

where

$$h(X_w, T) \neq 1 \text{ for some } T \in (T_2, T_3)$$

then equation (3.125) becomes

$$\delta^2 \ell\left[Q, \hat{C}_m, \lambda; 0, h, 0\right] = \int_{T_2}^{T_3} \frac{\partial^2 f}{\partial C^2}\left[T, Q(T), \hat{C}_m^{(3)}(X_w, T)\right]\left[h^{(3)}(X_w, T)\right]^2 dT \geq 0 \tag{3.132}$$

Applying Lemma 3 to equation (3.132) produces the necessary optimality condition,

$$\frac{\partial^2 f}{\partial C^2}\left[T, Q(T), \hat{C}_m^{(3)}(X_w, T)\right] \geq 0 \tag{3.133}$$

for all $T \in [T_2, T_3]$.

Notice from equation (3.23) that the second variation of ℓ with respect to λ is zero for all cases. Therefore, we apply the necessary conditions for optimality to the second variation of ℓ with respect to λ. Suppose $\hat{C}_m$ and $\hat{\lambda}$ are admissible and minimize ℓ then $\delta^2 \ell\left[Q, \hat{C}_m, \hat{\lambda}; 0, 0, \mu\right] = 0$ for all admissible variations μ. Additionally, note that equation (3.126) and equation (3.127) become

$$\frac{\partial^2}{\partial T_1^{\,2}} \ell = \frac{\partial f}{\partial T}\left[T_1, 1, \hat{C}_m^{(1)}(X_w, T_1)\right] - \frac{\partial f}{\partial T}\left[T_1, 0, \hat{C}_m^{(2)}(X_w, T_1)\right]$$

$$
+\int_{X_w}^{\infty}\hat{C}_m^{(1)}(X,T_1)\left\{\begin{aligned}&\frac{\partial^2\hat{\lambda}^{(1)}}{\partial T^2}(X,T_1)+\frac{\partial^2}{\partial X^2}\left[\frac{\partial\hat{\lambda}^{(1)}}{\partial T}(X,T_1)\left(\frac{1}{X}+D\right)\right]-\frac{\partial}{\partial X}\left[\frac{\partial\hat{\lambda}^{(1)}}{\partial T}(X,T_1)\left(\frac{1}{X}+\frac{D}{X}\right)\right]\\&-\beta\alpha\frac{\partial\hat{\lambda}^{(1)}}{\partial T}(X,T_1)+\alpha^3\beta e^{\alpha T_1}\left[\int_{T_1}^{T_2}e^{-\alpha t}\hat{\lambda}^{(2)}(X,t)\,dt+\int_{T_2}^{T_3}e^{-\alpha t}\hat{\lambda}^{(3)}(X,t)\,dt\right]\\&+\alpha^2\beta e^{\alpha T_1}\left[e^{-\alpha T_1}\hat{\lambda}^{(2)}(X,T_1)\right]\end{aligned}\right\}dX
$$

$$
-\int_{X_w}^{\infty}\hat{C}_m^{(2)}(X,T_1)\left\{\begin{aligned}&\frac{\partial^2\hat{\lambda}^{(2)}}{\partial T^2}(X,T_1)+\frac{\partial^2}{\partial X^2}\frac{\partial\hat{\lambda}^{(2)}}{\partial T}(X,T_1)D-\frac{\partial}{\partial X}\left[\frac{\partial\lambda^{(2)}}{\partial T}(X,T_1)\frac{D}{X}\right]\\&-\beta\alpha\frac{\partial\hat{\lambda}^{(2)}}{\partial T}(X,T_1)+\alpha^3\beta e^{\alpha T_1}\left[\int_{T_1}^{T_2}e^{-\alpha t}\hat{\lambda}^{(2)}(X,t)\,dt+\int_{T_2}^{T_3}e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\right]\\&-\alpha^2\beta e^{\alpha T_1}\left[e^{-\alpha T_1}\hat{\lambda}^{(2)}(X,T_1)\right]\end{aligned}\right\}dX
$$

$$
-D\hat{C}_m^{(1)}(\infty,T_1)\left[\frac{\partial\hat{\lambda}^{(1)}}{\partial T}(\infty,T_1)+\frac{\partial}{\partial X}\frac{\partial\hat{\lambda}^{(1)}}{\partial T}(\infty,T_1)\right]
$$

$$
+D\hat{C}_m^{(2)}(\infty,T_1)\left[\frac{\partial\hat{\lambda}^{(2)}}{\partial T}(\infty,T_1)+\frac{\partial}{\partial X}\frac{\partial\hat{\lambda}^{(2)}}{\partial T}(\infty,T_1)\right]
$$

$$
+\hat{C}_m^{(1)}(X_w,T_1)\left\{\frac{\partial}{\partial X}\frac{\partial\hat{\lambda}^{(1)}}{\partial T}(X_w,T_1)\left(\frac{1}{X_w}+D\right)-\frac{\partial\hat{\lambda}^{(1)}}{\partial T}(X_w,T_1)\left(\frac{1}{X_w}+\frac{D}{X_w}\right)-\frac{\partial\hat{\lambda}^{(1)}}{\partial T}(X_w,T_1)\frac{1}{{X_w}^2}\right\}
$$

$$
-\hat{C}_m^{(2)}(X_w,T_1)\left\{\frac{\partial}{\partial X}\frac{\partial\hat{\lambda}^{(2)}}{\partial T}(X_w,T_1)D-\frac{\partial\hat{\lambda}^{(2)}}{\partial T}(X_w,T_1)\frac{D}{X_w}\right\}\qquad(3.134)
$$

and

$$
\frac{\partial^2}{\partial {T_2}^2}\mathcal{L}=\frac{\partial f}{\partial T}\left[T_2,0,\hat{C}_m^{(2)}(X_w,T_2)\right]-\frac{\partial f}{\partial T}\left[T_2,1,\hat{C}_m^{(3)}(X_w,T_2)\right]
$$

$$
+\int_{X_w}^{\infty}\hat{C}_m^{(2)}(X,T_2)\left\{\begin{aligned}&\frac{\partial^2\hat{\lambda}^{(2)}}{\partial T^2}(X,T_2)+\frac{\partial^2}{\partial X^2}\frac{\partial\hat{\lambda}^{(2)}}{\partial T}(X,T_2)D-\frac{\partial}{\partial X}\left[\frac{\partial\hat{\lambda}^{(2)}}{\partial T}(X,T_2)\frac{D}{X}\right]\\&-\beta\alpha(X,T_2)\frac{\partial\hat{\lambda}^{(2)}}{\partial T}+\alpha^3\beta e^{\alpha T_2}\left[\int_{T_2}^{T_3}e^{-\alpha t}\hat{\lambda}^{(3)}(X,t)\,dt\right]\\&-\alpha^2\beta e^{\alpha T_2}\left(e^{-\alpha T_2}\hat{\lambda}^{(3)}(X,T_2)\right)\end{aligned}\right\}dX
$$

$$
-\int_{X_w}^{\infty}\hat{C}_m^{(3)}(X,T_2)\left\{\begin{array}{l}\dfrac{\partial^2\hat{\lambda}^{(3)}}{\partial T^2}(X,T_2)+\dfrac{\partial^2}{\partial X^2}\left[\dfrac{\partial\hat{\lambda}^{(3)}}{\partial T}(X,T_2)\left(\dfrac{1}{X}+D\right)\right]-\dfrac{\partial}{\partial X}\left[\dfrac{\partial\hat{\lambda}^{(3)}}{\partial T}(X,T_2)\left(\dfrac{1}{X}+\dfrac{D}{X}\right)\right]\\ -\beta\alpha\dfrac{\partial\hat{\lambda}^{(3)}}{\partial T}(X,T_2)+\alpha^3\beta e^{\alpha T_2}\int_{T_2}^{T_3}e^{-\alpha t}\hat{\lambda}^{(3)}(X,t)\,dt-\alpha^2\beta e^{\alpha T_2}\left(e^{-\alpha T_2}\hat{\lambda}^{(3)}(X,T_2)\right)\end{array}\right\}dX
$$

$$
-D\hat{C}_m^{(2)}(\infty,T_2)\left[\frac{\partial\hat{\lambda}^{(2)}}{\partial T}(\infty,T_2)+\frac{\partial}{\partial X}\frac{\partial\hat{\lambda}^{(2)}}{\partial T}(\infty,T_2)\right]
$$

$$
+D\hat{C}_m^{(3)}(\infty,T_2)\left[\frac{\partial\hat{\lambda}^{(3)}}{\partial T}(\infty,T_2)+\frac{\partial}{\partial X}\frac{\partial\hat{\lambda}^{(3)}}{\partial T}(\infty,T_2)\right]
$$

$$
+\hat{C}_m^{(2)}(X_w,T_2)\left\{\frac{\partial}{\partial X}\frac{\partial\hat{\lambda}^{(2)}}{\partial T}(X_w,T_2)D-\frac{\partial\hat{\lambda}^{(2)}}{\partial T}(X_w,T_2)\frac{D}{X_w}\right\}
$$

$$
-\hat{C}_m^{(3)}(X_w,T_2)\left\{\frac{\partial}{\partial X}\frac{\partial\hat{\lambda}^{(3)}}{\partial T}(X_w,T_2)\left(\frac{1}{X_w}+D\right)-\frac{\partial\hat{\lambda}^{(3)}}{\partial T}(X_w,T_2)\left(\frac{1}{X_w}+\frac{D}{X_w}\right)-\frac{\partial\hat{\lambda}^{(3)}}{\partial T}(X_w,T_2)\frac{1}{X_w^{\,2}}\right\}
$$

(3.135)

Notice that if

$$
F(T)=\hat{\lambda}(\infty,T)+\frac{\partial\hat{\lambda}}{\partial X}(\infty,T)=0 \tag{3.136}
$$

and since $\hat{\lambda}$ satisfies the boundary condition F(T)=0 for all $T\in[0,T_3]$ then

$$
\frac{dF}{dT}=0 \tag{3.137}
$$

Then for $T\neq 0$, T_1, T_2, or T_3 the differential equation holds true

$$
\begin{aligned}
&\frac{\partial}{\partial T}\left[\frac{\partial\hat{\lambda}}{\partial X}(X_w,T)\left(\frac{Q(T)}{X_w}+D\right)-\hat{\lambda}(X_w,T)\left(\frac{Q(T)}{X_w}+\frac{D}{X_w}\right)-\hat{\lambda}(X_w,T)\frac{Q(T)}{X_w^{\,2}}\right]\\
&\quad=-\frac{\partial}{\partial T}\left[\frac{\partial f}{\partial C}\left[T,Q(T),\hat{C}_m(X_w,T)\right]\right]\\
&\quad=-\frac{\partial^2 f}{\partial T\,\partial C}\left[T,Q(T),\hat{C}_m(X_w,T)\right]\hat{C}_m(X_w,T)\\
&\qquad-\left\{\frac{\partial^2 f}{\partial C^2}\left[T,Q(T),\hat{C}_m(X_w,T)\right]\frac{\partial\hat{C}_m}{\partial T}(X_w,T)\right\}\hat{C}_m(X_w,T)
\end{aligned} \tag{3.138}
$$

Equations (3.134) and (3.135) now simplify to

$$
\frac{\partial^2}{\partial T_1^{\,2}}\mathcal{L}=\frac{\partial f}{\partial T}\left[T_1,1,\hat{C}_m^{(1)}(X_w,T_1)\right]-\frac{\partial f}{\partial T}\left[T_1,0,\hat{C}_m^{(2)}(X_w,T_1)\right]
$$

$$
+\int_{X_w}^{\infty}\hat{C}_m^{(1)}(X,T_1)\left\{\begin{array}{l}\dfrac{\partial^2\hat{\lambda}^{(1)}}{\partial T^2}(X,T_1)+\dfrac{\partial^2}{\partial X^2}\left[\dfrac{\partial\hat{\lambda}^{(1)}}{\partial T}(X,T_1)\left(\dfrac{1}{X}+D\right)\right]-\dfrac{\partial}{\partial X}\left[\dfrac{\partial\hat{\lambda}^{(1)}}{\partial T}(X,T_1)\left(\dfrac{1}{X}+\dfrac{D}{X}\right)\right]\\ -\beta\alpha\dfrac{\partial\hat{\lambda}^{(1)}}{\partial T}(X,T_1)+\alpha^3\beta e^{\alpha T_1}\left[\int_{T_1}^{T_2}e^{-\alpha t}\hat{\lambda}^{(2)}(X,t)\,dt+\int_{T_2}^{T_3}e^{-\alpha t}\hat{\lambda}^{(3)}(X,t)\,dt\right]\\ -\alpha^2\beta e^{\alpha T_1}\left[e^{-\alpha T_1}\hat{\lambda}^{(2)}(X,T_1)\right]\end{array}\right\}dX
$$

$$
-\int_{X_w}^{\infty}\hat{C}_m^{(2)}(X,T_1)\left\{\begin{array}{l}\dfrac{\partial^2\hat{\lambda}^{(2)}}{\partial T^2}(X,T_1)+\dfrac{\partial^2}{\partial X^2}\dfrac{\partial\hat{\lambda}^{(2)}}{\partial T}(X,T_1)D-\dfrac{\partial}{\partial X}\left[\dfrac{\partial\hat{\lambda}^{(2)}}{\partial T}(X,T_1)\dfrac{D}{X}\right]\\ -\beta\alpha(X,T_1)\dfrac{\partial\hat{\lambda}^{(2)}}{\partial T}+\alpha^3\beta e^{\alpha T_1}\left[\int_{T_1}^{T_2}e^{-\alpha t}\hat{\lambda}^{(2)}(X,t)\,dt+\int_{T_2}^{T_3}e^{-\alpha t}\hat{\lambda}^{(3)}(X,t)\,dt\right]\\ -\alpha^2\beta e^{\alpha T_1}\left[e^{-\alpha T_1}\hat{\lambda}^{(2)}(X,T_1)\right]\end{array}\right\}dX
$$

$$
+\hat{C}_m^{(1)}(X_w,T_1)\left\{-\frac{\partial^2 f}{\partial T\,\partial C}\left[T_1,1,\hat{C}_m(X_w,T_1)\right]-\frac{\partial^2 f}{\partial C^2}\left[T_1,1,\hat{C}_m(X_w,T_1)\right]\frac{\partial\hat{C}_m}{\partial T}(X_w,T_1)\right\}
$$

$$
-\hat{C}_m^{(2)}(X_w,T_1)\left\{-\frac{\partial^2 f}{\partial T\,\partial C}\left[T_1,0,\hat{C}_m(X_w,T_1)\right]-\frac{\partial^2 f}{\partial C^2}\left[T_1,0,\hat{C}_m(X_w,T_1)\right]\frac{\partial\hat{C}_m}{\partial T}(X_w,T_1)\right\}
\tag{3.139}
$$

and

$$
\frac{\partial^2}{\partial T_2{}^2}\mathcal{L}=\frac{\partial f}{\partial T}\left[T_2,0,\hat{C}_m^{(2)}(X_w,T_2)\right]-\frac{\partial f}{\partial T}\left[T_2,1,\hat{C}_m^{(3)}(X_w,T_2)\right]
$$

$$
+\int_{X_w}^{\infty}\hat{C}_m^{(2)}(X,T_2)\left\{\begin{array}{l}\dfrac{\partial^2\hat{\lambda}^{(2)}}{\partial T^2}(X,T_2)+\dfrac{\partial^2}{\partial X^2}\dfrac{\partial\hat{\lambda}^{(2)}}{\partial T}(X,T_2)D-\dfrac{\partial}{\partial X}\left[\dfrac{\partial\hat{\lambda}^{(2)}}{\partial T}(X,T_2)\dfrac{D}{X}\right]\\ -\beta\alpha(X,T_2)\dfrac{\partial\hat{\lambda}^{(2)}}{\partial T}+\alpha^3\beta e^{\alpha T_2}\int_{T_2}^{T_3}e^{-\alpha t}\hat{\lambda}^{(3)}(X,t)\,dt\\ -\alpha^2\beta e^{\alpha T_2}\left(e^{-\alpha T_2}\hat{\lambda}^{(3)}(X,T_2)\right)\end{array}\right\}dX
$$

$$
-\int_{X_w}^{\infty}\hat{C}_m^{(3)}(X,T_2)\left\{\begin{array}{l}\dfrac{\partial^2\hat{\lambda}^{(3)}}{\partial T^2}(X,T_2)+\dfrac{\partial^2}{\partial X^2}\left[\dfrac{\partial\hat{\lambda}^{(3)}}{\partial T}(X,T_2)\left(\dfrac{1}{X}+D\right)\right]-\dfrac{\partial}{\partial X}\left[\dfrac{\partial\hat{\lambda}^{(3)}}{\partial T}(X,T_2)\left(\dfrac{1}{X}+\dfrac{D}{X}\right)\right]\\ -\beta\alpha\dfrac{\partial\hat{\lambda}^{(3)}}{\partial T}(X,T_2)+\alpha^3\beta e^{\alpha T_2}\int_{T_2}^{T_3}e^{-\alpha t}\hat{\lambda}^{(3)}(X,t)\,dt-\alpha^2\beta e^{\alpha T_2}\left(e^{-\alpha T_2}\hat{\lambda}^{(3)}(X,T_2)\right)\end{array}\right\}dX
$$

$$
+\hat{C}_m^{(2)}(X_w,T_2)\left\{-\frac{\partial^2 f}{\partial T\,\partial C}\left[T_2,0,\hat{C}_m(X_w,T_2)\right]-\frac{\partial^2 f}{\partial C^2}\left[T_2,0,\hat{C}_m(X_w,T_2)\right]\frac{\partial\hat{C}_m}{\partial T}(X_w,T_2)\right\}
$$

$$-\hat{C}_m^{(3)}(X_w,T_2)\left\{-\frac{\partial^2 f}{\partial T\partial C}\left[T_2,1,\hat{C}_m(X_w,T_2)\right]-\frac{\partial^2 f}{\partial C^2}\left[T_2,1,\hat{C}_m(X_w,T_2)\right]\frac{\partial \hat{C}_m}{\partial T}(X_w,T_2)\right\}$$

(3.140)

Notice from the first variation of $\mathcal{L}$ with respect to C (see equation 3.67) that

$$\frac{\partial\hat{\lambda}}{\partial T}+G^{*}\left[\hat{\lambda}\right]+\alpha^2\beta e^{\alpha T}\int_T^{T_{final}} e^{-\alpha t}\hat{\lambda}(X,t)\,dt=0 \tag{3.141}$$

So taking the derivative with respect to T yields

$$\frac{\partial^2\lambda}{\partial T^2}+G^{*}\left[\frac{\hat{\lambda}}{\partial T}\right]+\alpha^3\beta e^{\alpha T}\int_T^{T_{final}} e^{-\alpha t}\lambda(X,t)\,dt-\alpha^2\beta\lambda(X,T)=0 \tag{3.142}$$

Evaluation this equation at $T = T_1$ and $T = T_2$ and plugging into equations (3.139) and (3.140) gives

$$\begin{aligned}
\frac{\partial^2}{\partial T_1{}^2}\mathcal{L} &= \frac{\partial f}{\partial T}\left[T_1,1,\hat{C}_m^{(1)}(X_w,T_1)\right]-\frac{\partial f}{\partial T}\left[T_1,0,\hat{C}_m^{(2)}(X_w,T_1)\right]\\
&+\int_{X_w}^{\infty}\hat{C}_m^{(1)}(X,T_1)\left\{\alpha^2\beta\lambda^{(1)}(X,T_1)\right\}dX\\
&-\int_{X_w}^{\infty}\hat{C}_m^{(2)}(X,T_1)\left\{\alpha^2\beta\lambda^{(2)}(X,T_1)\right\}dX\\
&+\hat{C}_m^{(1)}(X_w,T_1)\left\{-\frac{\partial^2 f}{\partial T\partial C}\left[T_1,1,\hat{C}_m^{(1)}(X_w,T_1)\right]-\frac{\partial^2 f}{\partial C^2}\left[T_1,1,\hat{C}_m^{(1)}(X_w,T_1)\right]\frac{\partial\hat{C}_m^{(1)}}{\partial T}(X_w,T_1)\right\}\\
&-\hat{C}_m^{(2)}(X_w,T_1)\left\{-\frac{\partial^2 f}{\partial T\partial C}\left[T_1,0,\hat{C}_m^{(2)}(X_w,T_1)\right]-\frac{\partial^2 f}{\partial C^2}\left[T_1,0,\hat{C}_m^{(2)}(X_w,T_1)\right]\frac{\partial\hat{C}_m^{(2)}}{\partial T}(X_w,T_1)\right\}
\end{aligned}$$

(3.143)

and

$$\begin{aligned}
\frac{\partial^2}{\partial T_2{}^2}\mathcal{L} &= \frac{\partial f}{\partial T}\left[T_2,0,\hat{C}_m^{(2)}(X_w,T_2)\right]-\frac{\partial f}{\partial T}\left[T_2,1,\hat{C}_m^{(3)}(X_w,T_2)\right]\\
&+\int_{X_w}^{\infty}\hat{C}_m^{(2)}(X,T_2)\left\{\alpha^2\beta\lambda^{(2)}(X,T_2)\right\}dX\\
&-\int_{X_w}^{\infty}\hat{C}_m^{(3)}(X,T_2)\left\{\alpha^2\beta\lambda^{(3)}(X,T_2)\right\}dX
\end{aligned}$$

$$+\hat{C}_m^{(2)}(X_w,T_2)\left\{-\frac{\partial^2 f}{\partial T\partial C}\left[T_2,0,\hat{C}_m^{(2)}(X_w,T_2)\right]-\frac{\partial^2 f}{\partial C^2}\left[T_2,0,\hat{C}_m^{(2)}(X_w,T_2)\right]\frac{\partial \hat{C}_m^{(2)}}{\partial T}(X_w,T_2)\right\}$$

$$-\hat{C}_m^{(3)}(X_w,T_2)\left\{-\frac{\partial^2 f}{\partial T\partial C}\left[T_2,1,\hat{C}_m^{(3)}(X_w,T_2)\right]-\frac{\partial^2 f}{\partial C^2}\left[T_2,1,\hat{C}_m^{(3)}(X_w,T_2)\right]\frac{\partial \hat{C}_m^{(3)}}{\partial T}(X_w,T_2)\right\}$$

(3.144)

Notice that $\lambda^{(1)}(X_w,T_1) = \lambda^{(2)}(X_w,T_1)$ by continuity and similarly $\lambda^{(2)}(X_w,T_2) = \lambda^{(3)}(X_w,T_2)$. Equations (3.143) and (3.144) simplify to become

$$\frac{\partial^2}{\partial T_1^{\,2}}\mathcal{L} = \frac{\partial f}{\partial T}\left[T_1,1,\hat{C}_m^{(1)}(X_w,T_1)\right]-\frac{\partial f}{\partial T}\left[T_1,0,\hat{C}_m^{(2)}(X_w,T_1)\right]$$

$$+\hat{C}_m^{(1)}(X_w,T_1)\left\{-\frac{\partial^2 f}{\partial T\partial C}\left[T_1,1,\hat{C}_m^{(1)}(X_w,T_1)\right]-\frac{\partial^2 f}{\partial C^2}\left[T_1,1,\hat{C}_m^{(1)}(X_w,T_1)\right]\frac{\partial \hat{C}_m^{(1)}}{\partial T}(X_w,T_1)\right\}$$

$$-\hat{C}_m^{(2)}(X_w,T_1)\left\{-\frac{\partial^2 f}{\partial T\partial C}\left[T_1,0,\hat{C}_m^{(2)}(X_w,T_1)\right]-\frac{\partial^2 f}{\partial C^2}\left[T_1,0,\hat{C}_m^{(2)}(X_w,T_1)\right]\frac{\partial \hat{C}_m^{(2)}}{\partial T}(X_w,T_1)\right\}$$

(3.145)

and

$$\frac{\partial^2}{\partial T_2^{\,2}}\mathcal{L} = \frac{\partial f}{\partial T}\left[T_2,0,\hat{C}_m^{(2)}(X_w,T_2)\right]-\frac{\partial f}{\partial T}\left[T_2,1,\hat{C}_m^{(3)}(X_w,T_2)\right]$$

$$+\hat{C}_m^{(2)}(X_w,T_2)\left\{-\frac{\partial^2 f}{\partial T\partial C}\left[T_2,0,\hat{C}_m^{(2)}(X_w,T_2)\right]-\frac{\partial^2 f}{\partial C^2}\left[T_2,0,\hat{C}_m^{(2)}(X_w,T_2)\right]\frac{\partial \hat{C}_m^{(2)}}{\partial T}(X_w,T_2)\right\}$$

$$-\hat{C}_m^{(3)}(X_w,T_2)\left\{-\frac{\partial^2 f}{\partial T\partial C}\left[T_2,1,\hat{C}_m^{(3)}(X_w,T_2)\right]-\frac{\partial^2 f}{\partial C^2}\left[T_2,1,\hat{C}_m^{(3)}(X_w,T_2)\right]\frac{\partial \hat{C}_m^{(3)}}{\partial T}(X_w,T_2)\right\}$$

(3.146)

We now have the necessary optimality conditions for all cases when applied to the second variation of $\mathcal{L}$ with respect to arbitrary fixed functions $\hat{C}_m$ and $\hat{\lambda}$. Observe that if $\delta^2\mathcal{L}\left[Q,\hat{C}_m,\lambda;0,h,0\right]=0$ for all admissible variation h then $\hat{C}_m$ satisfies the following:

<u>Boundary Conditions</u>

$$\frac{\partial^2 f}{\partial C^2}\left[T,Q(T),\hat{C}_m(X_w,T)\right]\geq 0 \qquad (3.147)$$

for all $T \in [0, T_{final}]$

Lastly, notice that if $\hat{C}_m$ minimizes $\mathcal{L}$ then the second variation of $\mathcal{L}$ with respect to Q evaluated at $\hat{C}_m$ implies $\frac{\partial^2 \mathcal{L}}{\partial T_i^2}\left(\hat{T}_1, \hat{T}_2, \hat{C}_m, \lambda\right) \geq 0$ (for i = 1 and i = 2). Hence by ordinary calculus equations (3.145) and (3.146) become

$$
\begin{aligned}
\frac{\partial^2}{\partial T_1^2}\mathcal{L} = {} & \frac{\partial f}{\partial T}\left[\hat{T}_1, 1, \hat{C}_m^{(1)}\left(X_w, \hat{T}_1\right)\right] - \frac{\partial f}{\partial T}\left[\hat{T}_1, 0, \hat{C}_m^{(2)}\left(X_w, \hat{T}_1\right)\right] \\
& + \hat{C}_m^{(1)}\left(X_w, \hat{T}_1\right)\left\{-\frac{\partial^2 f}{\partial T \partial C}\left[\hat{T}_1, 1, \hat{C}_m^{(1)}\left(X_w, \hat{T}_1\right)\right] - \frac{\partial^2 f}{\partial C^2}\left[\hat{T}_1, 1, \hat{C}_m^{(1)}\left(X_w, \hat{T}_1\right)\right]\frac{\partial \hat{C}_m^{(1)}}{\partial T}\left(X_w, \hat{T}_1\right)\right\} \\
& - \hat{C}_m^{(2)}\left(X_w, \hat{T}_1\right)\left\{-\frac{\partial^2 f}{\partial T \partial C}\left[\hat{T}_1, 0, \hat{C}_m^{(2)}\left(X_w, \hat{T}_1\right)\right] - \frac{\partial^2 f}{\partial C^2}\left[\hat{T}_1, 0, \hat{C}_m^{(2)}\left(X_w, \hat{T}_1\right)\right]\frac{\partial \hat{C}_m^{(2)}}{\partial T}\left(X_w, \hat{T}_1\right)\right\} \geq 0
\end{aligned}
\tag{3.148}
$$

and

$$
\begin{aligned}
\frac{\partial^2}{\partial T_2^2}\mathcal{L} = {} & \frac{\partial f}{\partial T}\left[\hat{T}_2, 0, \hat{C}_m^{(2)}\left(X_w, \hat{T}_2\right)\right] - \frac{\partial f}{\partial T}\left[\hat{T}_2, 1, \hat{C}_m^{(3)}\left(X_w, \hat{T}_2\right)\right] \\
& + \hat{C}_m^{(2)}\left(X_w, \hat{T}_2\right)\left\{-\frac{\partial^2 f}{\partial T \partial C}\left[\hat{T}_2, 0, \hat{C}_m^{(2)}\left(X_w, \hat{T}_2\right)\right] - \frac{\partial^2 f}{\partial C^2}\left[\hat{T}_2, 0, \hat{C}_m^{(2)}\left(X_w, \hat{T}_2\right)\right]\frac{\partial \hat{C}_m^{(2)}}{\partial T}\left(X_w, \hat{T}_2\right)\right\} \\
& - \hat{C}_m^{(3)}\left(X_w, \hat{T}_2\right)\left\{-\frac{\partial^2 f}{\partial T \partial C}\left[\hat{T}_2, 1, \hat{C}_m^{(3)}\left(X_w, \hat{T}_2\right)\right] - \frac{\partial^2 f}{\partial C^2}\left[\hat{T}_2, 1, \hat{C}_m^{(3)}\left(X_w, \hat{T}_2\right)\right]\frac{\partial \hat{C}_m^{(3)}}{\partial T}\left(X_w, \hat{T}_2\right)\right\} \geq 0
\end{aligned}
\tag{3.149}
$$

Sufficient Optimality Conditions

Utilizing the procedure to determine the necessary optimality conditions for the second variation of $\mathcal{L}$ it was shown that if the functional $\mathcal{L}[Q, C_m, \lambda]$ is to have a minimum then certain quantities were nonnegative, was a necessary condition but not a sufficient condition. To obtain a sufficient optimality condition the following theorem is introduced:

> Theorem 2. *A sufficient condition for the functional* $J[y]$ *to have a minimum for* $y = \hat{y}$, *given that the first variation* $\delta J[\hat{y}; h]$ *vanishes for all admissible variation* h, *is that its second variation* $\delta^2 J[\hat{y}; h]$ *be strongly positive. That is,*

$\delta^2 J[\hat{y};h] \geq k\|h\|^2 > 0$ *for all admissible variations* h *for some constant* $k > 0$. *For a maximum*, $\delta^2 J[\hat{y};h] \leq k\|h\|^2 < 0$ (Gelfand & Fomin, 1963:100).

Suppose the first variation of $\mathcal{L}$ is zero for $\hat{Q}, \hat{C}_m$ and $\hat{\lambda}$. Suppose further that $\hat{Q}, \hat{C}_m$ and $\hat{\lambda}$ satisfy equation ((3.147), (3.148) and (3.149). Therefore, $\delta^2\mathcal{L}$ strongly positive implies from equations (3.147), (3.148) and (3.149) that

$$\frac{\partial^2 f}{\partial C^2}\left[T, \hat{Q}(T), \hat{C}_m(X_w, T)\right] > 0 \tag{3.150}$$

for all $T \in [0, T_{final}]$ and

$$\begin{aligned}
\frac{\partial^2}{\partial T_1^{\,2}}\mathcal{L} = {} & \frac{\partial f}{\partial T}\left[\hat{T}_1, 1, \hat{C}_m^{(1)}(X_w, T_1)\right] - \frac{\partial f}{\partial T}\left[\hat{T}_1, 0, \hat{C}_m^{(2)}(X_w, \hat{T}_1)\right] \\
& + \hat{C}_m^{(1)}(X_w, \hat{T}_1)\left\{-\frac{\partial^2 f}{\partial T \partial C}\left[\hat{T}_1, 1, \hat{C}_m^{(1)}(X_w, \hat{T}_1)\right] - \frac{\partial^2 f}{\partial C^2}\left[\hat{T}_1, 1, \hat{C}_m^{(1)}(X_w, \hat{T}_1)\right]\frac{\partial \hat{C}_m^{(1)}}{\partial T}(X_w, \hat{T}_1)\right\} \\
& - \hat{C}_m^{(2)}(X_w, \hat{T}_1)\left\{-\frac{\partial^2 f}{\partial T \partial C}\left[\hat{T}_1, 0, \hat{C}_m^{(2)}(X_w, \hat{T}_1)\right] - \frac{\partial^2 f}{\partial C^2}\left[\hat{T}_1, 0, \hat{C}_m^{(2)}(X_w, \hat{T}_1)\right]\frac{\partial \hat{C}_m^{(2)}}{\partial T}(X_w, \hat{T}_1)\right\} > 0
\end{aligned} \tag{3.151}$$

and

$$\begin{aligned}
\frac{\partial^2}{\partial T_2^{\,2}}\mathcal{L} = {} & \frac{\partial f}{\partial T}\left[\hat{T}_2, 0, \hat{C}_m^{(2)}(X_w, \hat{T}_2)\right] - \frac{\partial f}{\partial T}\left[\hat{T}_2, 1, \hat{C}_m^{(3)}(X_w, \hat{T}_2)\right] \\
& + \hat{C}_m^{(2)}(X_w, \hat{T}_2)\left\{-\frac{\partial^2 f}{\partial T \partial C}\left[\hat{T}_2, 0, \hat{C}_m^{(2)}(X_w, \hat{T}_2)\right] - \frac{\partial^2 f}{\partial C^2}\left[\hat{T}_2, 0, \hat{C}_m^{(2)}(X_w, \hat{T}_2)\right]\frac{\partial \hat{C}_m^{(2)}}{\partial T}(X_w, \hat{T}_2)\right\} \\
& - \hat{C}_m^{(3)}(X_w, \hat{T}_2)\left\{-\frac{\partial^2 f}{\partial T \partial C}\left[\hat{T}_2, 1, \hat{C}_m^{(3)}(X_w, \hat{T}_2)\right] - \frac{\partial^2 f}{\partial C^2}\left[\hat{T}_2, 1, \hat{C}_m^{(3)}(X_w, \hat{T}_2)\right]\frac{\partial \hat{C}_m^{(3)}}{\partial T}(X_w, \hat{T}_2)\right\} > 0
\end{aligned} \tag{3.152}$$

Summary

Within this chapter several issues have been addressed to ensure that the physics and mathematics utilized correctly meet the objective to create a management tool which will determine an optimized pulsed pumping schedule for aquifer remediation when contaminant transport is affected by rate-limited sorption/desorption. A calculus of variation approach was discussed briefly along with the aquifer characteristics and model assumptions. It was discovered that the class of bang-bang schedules required was not a convex set for the operation of the pumps. Additionally, an objective functional (in a general dimensionless form) was introduced to satisfy the management decision tool which addresses the pumping rate, contaminant concentration, and time variables. The development of the differential equations for contaminant transport were also modified.

Anticipating the need to solve the differential equations, a mathematical technique known as the Laplace transform was introduced and the differential equations were combined into one equation describing contaminant transport while the extraction pump is on and off. The concept of the constraint was introduced, where the Lagrangian multiplier incorporated the contaminant transport equation which provided all the elements to form the optimization problem.

With the optimization problem stated the necessary optimality conditions for the first variation was constructed and applied resulting in the requirement to satisfy equations (3.72) and (3.73). In order to solve these equations the necessity to solve the differential equations and evaluate the solution at the well was identified and the solutions in the Laplace domain resulted in the development of equations (3.95) and (3.123) for when the extraction well is on and off.

With the solutions to the differential equations and verification that an optimal solution exist, the second variation was constructed to determine the necessary optimality conditions for the second variation which would state whether or not the optimal solution was a maximum, minimum or neither. In addition, the sufficient optimality condition was introduced resulting in equations (3.150), (3.151) and (3.152).

The description of the mathematics creates the need to describe a procedure to further determine the optimal solution. Specifically, roots of the optimization problem will be found which will create candidate(s). Additional tests (i.e., the necessary and sufficient optimality conditions) will determine whether or not the candidates are a maxima or minima dependent on the management goal which is describe by the objective functional. The process is relatively simple to describe but may be somewhat challenging when applied to a specific management goal. For example, if the objective function (f) is independent of (T) that is, $f\left[Q(T), C_m(X_w, T)\right]$ then the optimization can be formulated as follows:

Minimize T_1 such that $0 \le T_1 \le T_{final}$ and

$$\mathcal{L}^{-1}\left[\overline{C}_m(X_w, s)\right]\Big|_{T=T_1} = \mathcal{C}^* \tag{3.153}$$

where $\mathcal{C}^* \in [0,1]$ is the smallest root of $J(\mathcal{C})$ and

$$J(\mathcal{C}) \equiv f(1,\mathcal{C}) - f(0,\mathcal{C}) - \mathcal{C}\left(\frac{\partial f}{\partial C}(1,\mathcal{C}) - \frac{\partial f}{\partial C}(0,\mathcal{C})\right) \tag{3.154}$$

Hence we seek zeros $\mathcal{C}^*$ of $J(\mathcal{C}) = 0$. If there exist some $\mathcal{C}^*$ between 0 and 1 then we seek a $\hat{T}_1$ such that

$$\mathcal{C}^* = \mathcal{L}^{-1}\left[\frac{e^{-\frac{1}{2}x}}{G[Ai]}\int_{x_w}^{\infty} Ai\left[\gamma^{\frac{1}{3}}\left(\xi + \frac{1}{4\gamma}\right)\right] e^{\frac{1}{2}\xi}\, \overline{F}(\xi, s)\, d\xi\right]_{T=\hat{T}_1} \tag{3.155}$$

Using $\hat{C}_m^{(1)}(X, \hat{T}_1)$ as initial data then we seek a $\hat{T}_2$ such that

$$\mathcal{C}^* = \mathcal{L}^{-1}\left[\overline{C}_m(X_w, s)\right]\Big|_{T=\hat{T}_2} \tag{3.156}$$

that is

$$\mathcal{C}^* = \mathcal{L}^{-1}\left[\frac{\tilde{\gamma}^{\frac{1}{2}}}{X_w K_o'\left(\tilde{\gamma}^{\frac{1}{2}} X_w\right)} \int_{X_w}^{\infty} \xi K_o\left(\tilde{\gamma}^{\frac{1}{2}} \xi\right) \overline{F}(\xi, s)\, d\xi\right]\Bigg|_{T=\hat{T}_2} \tag{3.157}$$

where $\overline{F}$ depends on $\hat{C}_m^{(1)}(X, \hat{T}_1)$ and not on $C_{m,0}$ and $C_{im,0}$. This will require the development of a numerical code that will first seek out candidates and then determine whether or not a candidate is strictly positive or negative dependent on the management goals. Chapter 4 will investigate the applications more thoroughly.

4. Applications

Introduction

This chapter will apply the findings from the mathematical development of Chapter 3. The class of functionals will be discussed and eight subclasses of functionals will be developed based upon the corresponding function, $f(T, Q(T), C_m(X_w, T))$. From these classes, general cases will be developed and evaluated analytically to determine the trivial and nontrivial classes of functionals. Additionally, nontrivial classes which require numerical analysis will be identified. Lastly, specific examples based on various management goals will also be developed and evaluated.

Before the various general cases can be developed, the class of functionals based on the general corresponding function $f(T, Q(T), C_m(X_w, T))$ requires development. Listed below are the eight combinations of the general corresponding function.

Table 4.1

Independent Variables versus Dependent Functions where Y = Yes and N = No

	Independent Variable Present		
	T	$Q(T)$	$C_m(X_w,T)$
Dependent Functions			
$f(T)$	Y	N	N
$f(Q(T))$	N	Y	N
$f(C_m(X_w,T))$	N	N	Y
$f(T,Q(T))$	Y	Y	N
$f(T, C_m(X_w,T))$	Y	N	Y
$f(Q(T), C_m(X_w,T))$	N	Y	Y
$f(T,Q(T), C_m(X_w,T))$	Y	Y	Y
f	N	N	N

General Classes of the Functional

Recall that if $\hat{Q}$ (i.e., $\hat{T}_1$ and $\hat{T}_2$) and $\hat{C}_m$ are optimal then the necessary optimality condition for the first variation reduces to the following equations

$$\begin{aligned}&f\left[\hat{T}_1,1,\hat{C}_m^{(1)}\left(X_w,\hat{T}_1\right)\right]-f\left[\hat{T}_1,0,\hat{C}_m^{(2)}\left(X_w,\hat{T}_1\right)\right]\\&-\hat{C}_m^{(1)}\left(X_w,\hat{T}_1\right)\frac{\partial f}{\partial C}\left[\hat{T}_1,1,\hat{C}_m^{(1)}\left(X_w,\hat{T}_1\right)\right]+\hat{C}_m^{(2)}\left(X_w,\hat{T}_1\right)\frac{\partial f}{\partial C}\left[\hat{T}_1,0,\hat{C}_m^{(2)}\left(X_w,\hat{T}_1\right)\right]=0\end{aligned}\tag{4.1}$$

and

$$\begin{aligned}&f\left[\hat{T}_2,0,\hat{C}_m^{(2)}\left(X_w,\hat{T}_2\right)\right]-f\left[\hat{T}_2,1,\hat{C}_m^{(3)}\left(X_w,\hat{T}_2\right)\right]\\&-\hat{C}_m^{(2)}\left(X_w,\hat{T}_2\right)\frac{\partial f}{\partial C}\left[\hat{T}_2,0,\hat{C}_m^{(2)}\left(X_w,\hat{T}_2\right)\right]+\hat{C}_m^{(3)}\left(X_w,\hat{T}_2\right)\frac{\partial f}{\partial C}\left[\hat{T}_2,1,\hat{C}_m^{(3)}\left(X_w,\hat{T}_2\right)\right]=0\end{aligned}\tag{4.2}$$

for a pulsed pumping schedule at times $\hat{T}_1$ and $\hat{T}_2$. Note that

$$\hat{C}_m^{(1)}\left(X_w,\hat{T}_1\right)=\hat{C}_m^{(2)}\left(X_w,\hat{T}_1\right)\tag{4.3}$$

and

$$\hat{C}_m^{(2)}\left(X_w,\hat{T}_2\right)=\hat{C}_m^{(3)}\left(X_w,\hat{T}_2\right)\tag{4.4}$$

by continuity, then equations (4.1) and (4.2) become

$$\begin{aligned}&f\left[\hat{T}_1,1,\hat{C}_m^{(1)}\left(X_w,\hat{T}_1\right)\right]-f\left[\hat{T}_1,0,\hat{C}_m^{(1)}\left(X_w,\hat{T}_1\right)\right]\\&-\hat{C}_m^{(1)}\left(X_w,\hat{T}_1\right)\left[\frac{\partial f}{\partial C}\left[\hat{T}_1,1,\hat{C}_m^{(1)}\left(X_w,\hat{T}_1\right)\right]-\frac{\partial f}{\partial C}\left[\hat{T}_1,0,\hat{C}_m^{(1)}\left(X_w,\hat{T}_1\right)\right]\right]=0\end{aligned}\tag{4.5}$$

and

$$\begin{aligned}&f\left[\hat{T}_2,0,\hat{C}_m^{(2)}\left(X_w,\hat{T}_2\right)\right]-f\left[\hat{T}_2,1,\hat{C}_m^{(2)}\left(X_w,\hat{T}_2\right)\right]\\&-\hat{C}_m^{(2)}\left(X_w,\hat{T}_2\right)\left[\frac{\partial f}{\partial C}\left[\hat{T}_2,0,\hat{C}_m^{(2)}\left(X_w,\hat{T}_2\right)\right]-\frac{\partial f}{\partial C}\left[\hat{T}_2,1,\hat{C}_m^{(2)}\left(X_w,\hat{T}_2\right)\right]\right]=0\end{aligned}\tag{4.6}$$

With the various functionals from Table (4.1) and the equations for the necessary optimality condition for the first variation, general cases can be evaluated for those functionals that provide candidates which minimize the optimization problem and support an interesting management goal.

Case 1: The Function f is not dependent on any variable. This particular case does not serve any particular management goal. In addition, the evaluation of equations (4.5) or (4.6) provides no candidates for the optimization problem, however, it is a combination of the general functional and should be addressed.

Case 2: The Function f is dependent on time i.e., f(T). In this case, equations (4.5) and (4.6) become

$$f\left[\hat{T}_1\right] - f\left[\hat{T}_1\right] = 0 \tag{4.7}$$

and

$$f\left[\hat{T}_2\right] - f\left[\hat{T}_2\right] = 0 \tag{4.8}$$

respectively. Notice that all values $\hat{T}_1$ and $\hat{T}_2$ are candidate solutions and hence require further investigation by addressing the necessary and sufficient optimality conditions for the second variation. Regardless, because there is no dependence on either $C_m(X_w, T)$ or $Q(T)$ this particular problem may not provide an interesting management objective.

Case 3: The Function f is dependent on the pumping rate i.e., f(Q(T)). In this case, equations (4.5) and (4.6) become

$$f[1] - f[0] = 0 \tag{4.9}$$

and

$$f[0] - f[1] = 0 \tag{4.10}$$

respectively. These particular equations have no solutions $\hat{T}_1$ and $\hat{T}_2$ and thus do not provide any candidate pumping schedules. However, if more information is known about the function f, a manager who is concerned only with the pumping schedule may be able to determine an optimal pumping schedule.

Case 4: The Function f is dependent on the concentration i.e., $f(C_m(X_w, T))$. In this case, equations (4.5) and (4.6) become

$$f\left[\hat{C}_m^{(1)}\left(X_w, \hat{T}_1\right)\right] - f\left[\hat{C}_m^{(1)}\left(X_w, \hat{T}_1\right)\right] = 0 \tag{4.11}$$

and

$$f\left[\hat{C}_m^{(2)}\left(X_w, \hat{T}_2\right)\right] - f\left[\hat{C}_m^{(2)}\left(X_w, \hat{T}_2\right)\right] = 0 \tag{4.12}$$

respectively. Again notice that all values $\hat{T}_1$ and $\hat{T}_2$ are solutions and hence are candidates for a pumping schedule and will require further investigation to determine which candidates yield a minimum. Additionally, further information about the function will be required to determine the necessary and sufficient optimality conditions for the optimization problem, since this function class is implicitly dependent on Q(T) (recall C_m depends on Q). This particular functional may be useful if a manager is interested only in the contaminant concentration at the well. However, notice if the management decision is to maximize the concentration of contaminant removed then it will be shown that the solution to the optimization problem would be to pump continually (i.e., turn the pump on and not turn off).

Case 5: The Function f is dependent on the pumping rate and time i.e., $f(T,Q(T))$. In this case, equations (4.5) and (4.6) become

$$f\left[\hat{T}_1, 1\right] - f\left[\hat{T}_1, 0\right] = 0 \tag{4.13}$$

and

$$f\left[\hat{T}_2,0\right]-f\left[\hat{T}_2,1\right]=0 \qquad (4.14)$$

respectively. For this particular problem we define

$$g(T)\equiv f\left[T,1\right]-f\left[T,0\right] \qquad (4.15)$$

and seek roots of g(T) in the interval $[0,T_3]$. The smallest root (between 0 and T_3) will be $\hat{T}_1$ and the next smallest root (between $\hat{T}_1$ and T_3) will be $\hat{T}_2$. If no roots exist, then $\hat{T}_1$ may be equal to zero or T_3, by definition. Further analysis is needed to determine whether to leave the pump on or off. Since *f* is dependent on Q(T) this particular problem may provide a manager a more realistic goal to optimize pumping and may pose interesting management goal.

Case 6: The Function f is dependent on concentration and time i.e., $f(T, C_m(X_w, T))$. In this case, equations (4.5) and (4.6) become

$$f\left[\hat{T}_1,\hat{C}_m^{(1)}\left(X_w,\hat{T}_1\right)\right]-f\left[\hat{T}_1,\hat{C}_m^{(1)}\left(X_w,\hat{T}_1\right)\right]=0 \qquad (4.16)$$

and

$$f\left[\hat{T}_2,\hat{C}_m^{(2)}\left(X_w,\hat{T}_2\right)\right]-f\left[\hat{T}_2,\hat{C}_m^{(2)}\left(X_w,\hat{T}_2\right)\right]=0 \qquad (4.17)$$

respectively. Similar to case 4, notice that all values $\hat{T}_1$ and $\hat{T}_2$ are candidates and will require further investigation to determine which candidates are a minima. Additionally, further information about the function will be required to determine the necessary and sufficient optimality conditions for the optimization problem, since $C_m(X_w,T)$ is implicitly dependent on Q(T). This particular functional is more interesting than case 4 but is related and may be useful for a management decision dependent on both the clean-up time and the contaminant concentration at the well.

Case 7: The Function f is dependent on concentration and pumping rate i.e., $f(Q(T), C_m(X_w, T))$. In this case, equations (4.5) and (4.6) become,

$$\begin{aligned} & f\left[1,\hat{C}_m^{(1)}\left(X_w,\hat{T}_1\right)\right]-f\left[0,\hat{C}_m^{(1)}\left(X_w,\hat{T}_1\right)\right] \\ & -\hat{C}_m^{(1)}\left(X_w,\hat{T}_1\right)\left[\frac{\partial f}{\partial C}\left[1,\hat{C}_m^{(1)}\left(X_w,\hat{T}_1\right)\right]-\frac{\partial f}{\partial C}\left[0,\hat{C}_m^{(1)}\left(X_w,\hat{T}_1\right)\right]\right]=0 \end{aligned} \tag{4.18}$$

and

$$\begin{aligned} & f\left[0,\hat{C}_m^{(2)}\left(X_w,\hat{T}_2\right)\right]-f\left[1,\hat{C}_m^{(2)}\left(X_w,\hat{T}_2\right)\right] \\ & -\hat{C}_m^{(2)}\left(X_w,\hat{T}_2\right)\left[\frac{\partial f}{\partial C}\left[0,\hat{C}_m^{(2)}\left(X_w,\hat{T}_2\right)\right]-\frac{\partial f}{\partial C}\left[1,\hat{C}_m^{(2)}\left(X_w,\hat{T}_2\right)\right]\right]=0 \end{aligned} \tag{4.19}$$

respectively. This particular problem was introduced in Chapter 3 in general form as an example to motivate Chapter 4, however, for the continuity of this section it is reintroduced along with a procedure to determine the optimal solution.

Notice that both equations (4.18) and (4.19) need to be solved for the roots so that candidate pumping schedule(s) can be determined. Prior to identifying the candidates, additional tests (i.e., the necessary and sufficient optimality conditions) will be required to determine if the candidates minimize the optimization problem. If the analysis indicates that necessary and/or sufficient optimality conditions are met then the concentration of the contaminant at the well must be solved in the time domain. Recall that the governing equations and solutions for sorbing solute contaminant transport were solved in the Laplace domain for conditions when the extraction well is on and off in Chapter 3. Therefore, we seek a $\hat{T}_1$ such that $0 \le \hat{T}_1 \le T_3$ and

$$\hat{C}_m(X_w,\hat{T}_1)=\mathcal{L}^{1}\left[\overline{C}_m(X_w,s)\right]\Big|_{T=\hat{T}_1}=\mathcal{C}_1^* \tag{4.20}$$

that is

$$\hat{C}_m(X_w,\hat{T}_1)=\mathcal{L}^{1}\left[\frac{e^{-\frac{1}{2}x}}{G[Ai]}\int_{X_w}^{\infty}A\left[\left(\xi+\frac{1}{4\gamma}\right)\right]e^{\frac{1}{2}\xi}\,\overline{F}(\xi,s)\,d\xi\right]\Bigg|_{T=\hat{T}_1}=\mathcal{C}_1^* \tag{4.21}$$

where $\mathcal{C}_1^*$ is the smallest root (between 0 and 1) of the function

$$J[\mathcal{C}]\equiv f(1,\mathcal{C})-f(0,\mathcal{C})-\mathcal{C}\left[\frac{\partial f}{\partial \mathcal{C}}(1,\mathcal{C})-\frac{\partial f}{\partial \mathcal{C}}(0,\mathcal{C})\right] \tag{4.22}$$

Then we seek a $\hat{T}_2$ such that $\hat{T}_1<\hat{T}_2\leq T_3$ and

$$\hat{C}_m(X_w,\hat{T}_2)=\mathcal{L}^{1}\left[\overline{C}_m(X_w,s)\right]\Big|_{T=\hat{T}_2}=\mathcal{C}_2^* \tag{4.23}$$

where $\mathcal{C}_2^*$ is the next smallest root (between 0 and 1) of $J(\mathcal{C})=0$. That is,

$$\hat{C}_m(X_w,\hat{T}_2)=\mathcal{L}^{1}\left[\frac{\tilde{\gamma}^{\frac{1}{2}}}{X_w K_o'\left(\tilde{\gamma}^{\frac{1}{2}}X_w\right)}\int_{X_w}^{\infty}\xi K_o\left(\tilde{\gamma}^{\frac{1}{2}}\xi\right)\overline{F}(\xi,s)\,d\xi\right]\Bigg|_{T=\hat{T}_2}=\mathcal{C}_2^*$$

(4.24)

If no $\mathcal{C}_2^*$ exists in (0,1) then $=\hat{T}_2\,T_3$ by definition.

Notice, that $\overline{F}(\xi,s)$ is dependent on $\hat{C}_m^{(1)}(X_w,\hat{T}_1)$. Completion of this analysis will require the development of a numerical code that will first invert the Laplace solution of the concentration at the well for when the well is on and off. These results then can be utilized to seek out $\hat{T}_1$ and $\hat{T}_2$, and then determine whether or not the sufficient optimality condition is satisfied in order to meet the management objective.

This particular problem may prove to be a very interesting objective functional case, since there is dependence on both the contaminant concentration and the pumping schedule. In particular, a functional can be constructed that can maximize the amount of contaminant removed while minimizing the amount of water removed.

Case 8: The Function f is dependent on concentration, time and pumping rate i.e., $f(T,Q(T),C_m(X_w,T))$. In this case, equations (4.5) and (4.6) do not change, that is,

$$\begin{aligned}&f\left[\hat{T}_1,1,\hat{C}_m^{(1)}(X_w,\hat{T}_1)\right]-f\left[\hat{T}_1,0,\hat{C}_m^{(1)}(X_w,\hat{T}_1)\right]\\&-\hat{C}_m^{(1)}(X_w,\hat{T}_1)\left[\frac{\partial f}{\partial C}\left[\hat{T}_1,1,\hat{C}_m^{(1)}(X_w,\hat{T}_1)\right]-\frac{\partial f}{\partial C}\left[\hat{T}_1,0,\hat{C}_m^{(1)}(X_w,\hat{T}_1)\right]\right]=0\end{aligned} \tag{4.25}$$

and

$$\begin{aligned}&f\left[\hat{T}_2,0,\hat{C}_m^{(2)}(X_w,\hat{T}_2)\right]-f\left[\hat{T}_2,1,\hat{C}_m^{(2)}(X_w,\hat{T}_2)\right]\\&-\hat{C}_m^{(2)}(X_w,\hat{T}_2)\left[\frac{\partial f}{\partial C}\left[\hat{T}_2,0,\hat{C}_m^{(2)}(X_w,\hat{T}_2)\right]-\frac{\partial f}{\partial C}\left[\hat{T}_2,1,\hat{C}_m^{(2)}(X_w,\hat{T}_2)\right]\right]=0\end{aligned} \tag{4.26}$$

This particular class of functionals is the most interesting because it addresses all independent variables. Chapter 3 was dedicated to the solution of this problem and can be applied to the other 6 cases as observed with the first variation test. Like case 7 this particular class of functionals would require numerical analysis to identify the candidates for the optimization problem and would follow the same general procedure described to evaluate the first variation for necessary optimality conditions and the second variation for necessary and sufficient optimality conditions.

Summary. It has been observed that four of the eight functional cases may prove to be useful management objectives when developing objective functionals for pulsed pumping groundwater remediation when affected by rate-limited sorption/desorption. Also, note that the eight classes of functionals can be grouped into four common groups, since they are closely related and their analysis is similar (see Table 4.2).

Table 4.2

Grouped Classes of Functionals

	Groups			
	Group 1	Group 2	Group 3	Group 4
Class of Functionals	$f(T)$	$f(T, C_m(X_w,T))$	$f(Q(t),C_m(X_w,T))$	$f(T,Q(t),C_m(X_w,T))$
	$f(T,Q(t))$	$f(C_m(X_w,T))$		
	$f(Q(T))$			

Observe that groups dependent on $C_m(X_w,T)$ are the most interesting from a management prospective (i.e., groups two, three, and four). Even though group two seems interesting their solutions are trivial. Additionally, two of the three classes of functionals in group one have trivial solutions but $f(T,Q(T))$ is not trivial because of it's dependence on the function $Q(T)$, however, neither provide an interesting class of functionals. Only groups three and four are both interesting and non-trivial.

Specific Examples of Functionals

The previous section developed and evaluated general functional cases analytically and identified classes of functionals that can provide candidates to minimize the optimization problem and support potential management goals. This section will give specific examples of functionals given in the previous section by developing specific objective functionals (i.e., the function $f(T, Q(T), C_m(X_w, T))$ will be given) which represent the general class of functionals in groups two, three, and four. These functionals will be evaluated analytically and compared to the appropriate corresponding general functional case.

Example 1: Maximize the average contaminant concentration removed to a particular standard. Where the average contaminant concentration removed during a period of time above a regulatory standard is directly compared to the average contaminant concentration removed below the regulatory standard. This problem can be stated as follows,

minimize $$\Im[C] = \frac{1}{T_{final}} \int_0^{T_{final}} [C_s - C_m(X_w, T)] dT \tag{4.27}$$

over the admissible set of pumping schedules, subject to the constraints, initial conditions and boundary conditions described in Chapter 3, where C_s is a regulatory standard (i.e., a positive constant). The corresponding function is

$$f(C_m(X_w, T)) = \frac{C_s - C_m(X_w, T)}{T_{final}} \tag{4.28}$$

Applying the necessary optimality condition for the first variation equation (4.1) results in

$$J[\mathcal{C}] \equiv 0 \tag{4.29}$$

which correlates with the results from the general class $f(C_m(X_w, T))$ and implies that all values of $\hat{T}_1$ and $\hat{T}_2$ are candidates, stating that all schedules are candidates. Additionally, when the necessary optimality condition for the second variation, equations (3.148) and

(3.149), is applied to this objective functional the result is the zero function, again stating that all schedules are candidates. However, when the sufficient optimality condition is tested, equations (3.150), (3.151), and (3.152), and the answer is inconclusive, then it is unknown if the candidates will produce a maximum, a minimum or neither. Other tests will be needed to answer this question.

Example 2: Maximize the variance of the contaminant concentration removed compared to a particular standard. Since example 1 may have many fluctuations between times when the contaminant concentration is above and below the regulatory standard the amount of deviation from the standard may be important. This problem can be stated as follows,

minimize
$$\Im[C] = \frac{1}{T_{final}} \int_0^{T_{final}} \left[C_s - C_m(X_w, T)\right]^2 dT \tag{4.30}$$

over the admissible set of pumping schedules, subject to the constraints, initial conditions and boundary conditions described in Chapter 3, where C_s is a regulatory standard (i.e., a positive constant). The corresponding function is

$$f(C_m(X_w, T)) = \frac{\left[C_s - C_m(X_w, T)\right]^2}{T_{final}} \tag{4.31}$$

Applying the necessary optimality condition for the first variation, equation (4.5), results in

$$J[\mathcal{C}] \equiv 0 \tag{4.32}$$

Again, this correlates with the results from the general class $f(C_m(X_w,T))$ and implies that all values $\hat{T}_1$ and $\hat{T}_2$ between 0 and T_3 are candidates, stating that all schedules are candidates. However, when the necessary optimality condition for the second variation is applied to this objective functional, equations (3.148) and (3.149) become,

$$2C_m\left(X_w,\hat{T}_1\right)\left[\frac{\partial C_m^{(2)}}{\partial T}\left(X_w,\hat{T}_1\right)-\frac{\partial C_m^{(1)}}{\partial T}\left(X_w,\hat{T}_1\right)\right]\geq 0 \qquad (4.33)$$

and

$$2C_m\left(X_w,\hat{T}_2\right)\left[\frac{\partial C_m^{(3)}}{\partial T}\left(X_w,\hat{T}_2\right)-\frac{\partial C_m^{(2)}}{\partial T}\left(X_w,\hat{T}_2\right)\right]\geq 0 \qquad (4.34)$$

Interestingly, a criteria is established in order for the optimization problem to be minimized, where

$$\frac{\partial C_m^{(2)}}{\partial T}\left(X_w,\hat{T}_1\right)\geq\frac{\partial C_m^{(1)}}{\partial T}\left(X_w,\hat{T}_1\right) \qquad (4.35)$$

must be satisfied before turning the pump off and

$$\frac{\partial C_m^{(3)}}{\partial T}\left(X_w,\hat{T}_2\right)\geq\frac{\partial C_m^{(2)}}{\partial T}\left(X_w,\hat{T}_2\right) \qquad (4.36)$$

must be satisfied before turning the pump back on. When the sufficient optimality condition is tested, equations (3.150), (3.151) and (3.152), the result is similar to equations (4.33) and (4.34), however, they are strictly positive as shown below,

$$2C_m\left(X_w,\hat{T}_1\right)\left[\frac{\partial C_m^{(2)}}{\partial T}\left(X_w,\hat{T}_1\right)-\frac{\partial C_m^{(1)}}{\partial T}\left(X_w,\hat{T}_1\right)\right]>0 \qquad (4.37)$$

and

$$2C_m\left(X_w,\hat{T}_2\right)\left[\frac{\partial C_m^{(3)}}{\partial T}\left(X_w,\hat{T}_2\right)-\frac{\partial C_m^{(2)}}{\partial T}\left(X_w,\hat{T}_2\right)\right]>0 \qquad (4.38)$$

Note that applying the sufficient optimality condition imposes a more strict constraint which requires the following criteria to be met if the optimization problem is to be minimized where,

$$\frac{\partial C_m^{(2)}}{\partial T}\left(X_w, \hat{T}_1\right) > \frac{\partial C_m^{(1)}}{\partial T}\left(X_w, \hat{T}_1\right) \tag{4.39}$$

must be satisfied before turning the pump off and

$$\frac{\partial C_m^{(3)}}{\partial T}\left(X_w, \hat{T}_2\right) > \frac{\partial C_m^{(2)}}{\partial T}\left(X_w, \hat{T}_2\right) \tag{4.40}$$

must be satisfied before turning the pump back on. These necessary and sufficient optimality conditions motivate the need to have the solution $C_m(X_w,T)$ at the well as described earlier in this chapter.

Example 3: Maximize the amount of contaminant mass removed and minimize the amount of water mass removed. This problem can be stated as follows:

minimize $$\Im[Q] = (1-z)\int_0^{t_3} \rho_w\, Q'(t)\,dt - z\int_0^{t_3} Q'(t)\,C_m'(r_w, t)\,dt \tag{4.41}$$

Notice that this problem is stated in dimensional form where ρ_w is equivalent to the concentration of water measured at the well. A weighting factor ($0 < z < 1$) is introduced due to the large difference between the mass of contaminant and the mass of fluid pumped out of the aquifer. To create a dimensionless form of the optimization problem, the following variables and parameters are used (see Appendix 1 for more details).

$$X = \frac{r}{a_1} \tag{4.42}$$

$$T = \frac{Q_{max}\, t}{2\pi b\,\theta_m\, a_1^{\,2} R_m} \tag{4.43}$$

$$Q'(t) = Q_{max} Q(T) \tag{4.44}$$

$$C'_m(r,t) = C'_0 C_m(X,T) \tag{4.45}$$

Substituting the appropriate variables and parameters into equation (4.41) yields

$$\Im[Q] = (1-z)\rho_w \int_0^{T_3} Q(T) 2\pi b \theta_m a_l^2 R_m \, dT - z\int_0^{T_3} Q(T) C'_0 C_m(X_w, T) 2\pi b \theta_m a_l^2 R_m dT \tag{4.46}$$

$$\Im[Q] = 2\pi b \theta_m a_l^2 R_m \left[(1-z)\rho_w \int_0^{T_3} Q(T)\, dT - z\int_0^{T_3} Q(T) C'_0 C_m(X_w, T)\, dT \right] \tag{4.47}$$

factoring out C'_0 yields

$$\Im[Q] = 2\pi b \theta_m a_l^2 R_m C'_0 \left[(1-z)\frac{\rho_w}{C'_0} \int_0^{T_3} Q(T)\, dT - z\int_0^{T_3} Q(T) C_m(X_w, T)\, dT \right] \tag{4.48}$$

Let $K = 2\pi b \theta_m a_l^2 R_m C'_0$ then

$$\Im[Q] = K\left[(1-z)\frac{\rho_w}{C'_0} \int_0^{T_3} Q(T)\, dT - z\int_0^{T_3} Q(T) C_m(X_w, T)\, dT \right] \tag{4.49}$$

or

$$\Im[Q] = Kz\left[\left(\frac{1}{z} - 1\right)\frac{\rho_w}{C'_0} \int_0^{T_3} Q(T)\, dT - \int_0^{T_3} Q(T) C_m(X_w, T)\, dT \right] \tag{4.50}$$

If the minimum of $\Im[Q]$ occurs at $\hat{Q}$ then $\frac{1}{Kz}\Im[Q]$ is a minimum at $\hat{Q}$, therefore consider

$$\frac{1}{Kz}\Im[Q] = \left(\frac{1}{z} - 1\right)\frac{\rho_w}{C'_0} \int_0^{T_3} Q(T)\, dT - \int_0^{T_3} Q(T) C_m(X_w, T)\, dT \tag{4.51}$$

Substituting equation (4.51) with

$$u = \left(\frac{1}{z} - 1\right)\frac{\rho_w}{C'_0} \tag{4.52}$$

results in the dimensionless form of equation (4.41), so the optimization problem can be stated as,

minimize $$\Im_u[Q] = u\int_0^{T_3} Q(T)\,dT - \int_0^{T_3} Q(T)\,C_m(X_w, T)\,dT \tag{4.53}$$

for the parameter u such that $0 < u < \infty$, over the admissible set of pumping schedules, subject to the constraints, initial conditions, and boundary conditions described in Chapter 3. The corresponding function is,

$$f_u\big(Q(T), C_m(X_w, T)\big) = uQ(T) - Q(T)\,C_m(X_w, T) \tag{4.54}$$

Applying the necessary optimality condition for the first variation, equation (4.1) results in

$$J_u[\mathcal{C}] \equiv u \tag{4.55}$$

for all $0 < u < \infty$, which implies there are no roots. Therefore, we test to see if the pump is always on or off. Revisiting the optimization problem equation (4.53) and evaluating it for when the pump is off for all time, that is $Q(T) = 0$, results in

$$\Im_u[0] = 0 \tag{4.56}$$

for all $u \in (0, \infty)$ and when the pump is on for all time, that is $Q(T) = 1$, then

$$\Im_u[1] = T_3\left[u - \frac{1}{T_3}\int_0^{T_3} C_m(X_w, T)\,dT\right] \tag{4.57}$$

Observe that equations (4.56) and (4.57) result in the following decision Table (4.3).

Table 4.3

Management Decision when the Weighting Factor is 0 and Very Large

u	Functional Comparison	Choose Q(T) =
0	$\Im_0[1] < \Im_0[0]$	1
∞	$\Im_\infty[1] > \Im_\infty[0]$	0

If the weighting factor (u) is zero the removal of contaminant mass is of most interest to the manager. Therefore, the management decision would be to pump constantly. Conversely, if the weighting factor (u) is very large, the removal of contaminant is trivial and the management decision would be to never pump. Also note that additional tests (i.e., necessary and sufficient optimality conditions) are not needed. In addition, the necessity to solve for both $C_m(X_w,T)$ at the well when the pump is on and off is not required as described in the procedure in Case 7.

Example 4: Maximize the contaminant mass removed while considering the future and net present value of the project. Utilizing the dimensionless derivation in the previous example the following problem can be stated as:

Minimize $$\Im_u[Q] = \int_0^{T_3} e^{\varepsilon T}\left[uQ(T) - Q(T)C_m(X_w, T)\right]dT \tag{4.58}$$

for the parameter u such that $0 < u < \infty$, over the admissible set of pumping schedules, subject to the constraints, initial conditions, and boundary conditions described in Chapter 3. Here $e^{\varepsilon T}$ is approximately equivalent to the present value equation described below,

$$P = \frac{F}{(1+\varepsilon)^n} \tag{4.59}$$

where

P describes the present worth or value

F describes the future value

ε describes the interest rate or discount rate

n describes the number of periods

and would have units of dollars • mass of contaminant (i.e., the amount of money required to remove contaminant mass). Notice that the functional described which depends on T, Q, and C_m but can be represented as the product of two functions, A(T) and B(Q(T), $C_m(X_w,T)$). This simplification results in the corresponding function described below,

$$f(T, Q(T), C_m(X_w, T)) = e^{\varepsilon T}\left[uQ(T) - Q(T)C_m(X_w, T)\right] \tag{4.60}$$

Applying the necessary optimality condition for the first variation, equation (4.1), results in

$$e^{\varepsilon T}\left(u - C_m\left(X_w, \hat{T}_1\right)\right) + e^{\varepsilon T} C_m\left(X_w, \hat{T}_1\right) = 0 \tag{4.61}$$

which simplifies to

$$e^{\varepsilon T} u = 0 \tag{4.62}$$

Observing that $e^{\varepsilon T} \neq 0$ then

$$J_u[\mathcal{C}] = u \tag{4.63}$$

for all $0 < u < \infty$, which implies there are no roots. Therefore, we test to see if the pump is always on or off. Evaluating the problem further results in

$$\Im_u[0] = 0 \tag{4.64}$$

for all $u \in (0, \infty)$ and

$$\Im_u[1] = T_3\left[u - \frac{1}{T_3}\int_0^{T_3} C_m(X_w, T)\,dT\right] \tag{4.65}$$

when the pump is strictly on for all time $0 \leq T \leq T_3$, as in Example 3, where the management decisions represented in Table 4.3 are appropriate.

Summary

This chapter applied the findings from Chapter 3 and identified eight subclasses of functionals. Of the eight subclasses it was identified that the corresponding function f(T, Q(T)) was nontrivial and non-interesting, the corresponding functions $f(T, C_m(X_w,T))$ and $f(C_m(X_w,T))$ were trivial and interesting, but most importantly the corresponding functions $f(Q(T),C_m(X_w,T))$ and $f(T,Q(T),C_m(X_w,T))$ were interesting and nontrivial from a management perspective for groundwater remediation when contaminant transport is affected by rate-limited sorption. Specific examples were then evaluated and confirmed the results of the general cases. Additionally, the analytical solutions provided management decisions for either a pulsed pumping, continuous pumping strategy, or not to pump at all for specific objective functionals.

5. Conclusions and Recommendations

This concluding chapter pulls together the research presented in the previous chapters. It begins with a summary of the first two chapters and focuses on the findings presented in both chapters three and four. It will discuss the significance of the findings and the practical implications of the results. Lastly, it lists recommendations for follow-on efforts to this research.

Summary

The remediation of groundwater contamination continues to persist as a social and economic problem due to increased governmental regulations and public health concerns. Additionally, the geochemistry of the aquifer and the contaminant transport within the aquifer complicates the remediation process to restore contaminated aquifers to conditions compatible with health-based standards. Currently, the preferred method for aquifer cleanup (pump-and-treat) has several limitations including, the persistence of sorbed chemicals on soil matrix and the long term operation and maintenance expense. The impetus of this research was to demonstrate that a calculus of variations approach could be applied to a pulsed pumping aquifer remediation problem where contaminant transport was affected by rate-limited sorption and to answer several management objectives.

The literature search revealed that the affect of rate-limited sorption still presents difficulties for the manager interested in groundwater remediation. It addressed the most current development of aquifer models to describe this phenomena and identified optimal pumping strategies. It was observed that several aquifer remediation methods involved optimization techniques but none addressed the affect of rate limited sorption.

Additionally, the literature review revealed that no one to date has developed an optimization technique involving pulsed pumping nor a method that involves an analytical approach (i.e., a calculus of variation approach).

Summary of Findings

In this research several complex problems were collectively addressed into a specific aquifer remediation problem to demonstrate the untapped power of a mathematical technique. First, a pulsed pumping method was utilized since it was observed as the most promising strategy to address the optimization problem. Secondly, the affect of rate-limited sorption was introduced to test the concept of the constraint where the Lagrange multiplier incorporated the contaminant transport equation. Lastly, a class of functionals was developed and discussed as management objectives that would give insight to both the social and economic problems of aquifer remediation. Below are a list of findings.

(1) Chapter 3 revealed that a calculus of variations approach to optimize the specific functional when pulsed pumping aquifer remediation is affected by rate-limited sorption is feasible.

(2) Chapter 4 identified eight subclasses of functionals. When the objective functional was dependent on the contaminant concentration and was in the form of a quadratic a criteria for when the pump should be turned on or off is observed, verifying a pulsed pumping strategy. However, when the objective function f is linear in the concentration then the decision is bivariate (i.e., either turn the pump on for all time or do not turn the pump on at all).

(3) Specific examples verified the general class of functionals (i.e., if the form the function is known the outcome is also known) which may provide insight to the manager to make rational decisions.

(4) Additionally, the analytic solutions presented in this research may be useful in verifying numerical codes developed to solve optimal pulsed pumping aquifer remediation problems under conditions of rate-limited sorption.

Recommendations

As identified in Chapter 3 and Chapter 4, not all problems can be solved analytically and require the development of a numerical code to invert the contaminant concentration solution at the well in the Laplace domain to the time domain. Additionally, this research only addressed a schedule that would go through three stages (e.g., the extraction pump is on, off, on). Currently, these two issues present limiting factors for immediate follow-on research where the creation of a numerical code can resolve these short term issues. Future continuation of this research should focused on the following areas:

(1) Create a more realistic scenario and eliminate the model assumptions described in Chapter 3.

(2) Allow for multiple extraction wells, whose pumping rate schedules could differ and seek an optimal pumping schedule for each well.

(3) Investigate the placement of multiple extraction wells and seek an optimal placement and optimal pumping schedules.

(4) Validate theoretical results with experimental results obtained from sand box experiments and/or field experiments.

Appendix A

This appendix contains the derivation of the advection-dispersion equation that governs the contaminant transport in a saturated, homogeneous porous media with radial converging flow. It incorporates a source/sink term to describe the transfer of contaminant from the aqueous phase to immobile water regions, and accounts for the distribution of contaminant between aquifer solids and groundwater (Adams & Viramontes, 1993).

$$\frac{\partial C'_m(r,t)}{\partial t} = \frac{1}{R_m}\frac{1}{r}\frac{\partial}{\partial r}\left[rD'_m\frac{\partial C'_m(r,t)}{\partial r}\right] - \frac{V'_m(r)}{R_m}\frac{\partial C'_m(r,t)}{\partial r} - \beta\frac{\partial C'_{im}(r,t)}{\partial t} \quad \text{(A.1)}$$

Where the following are defined as

$$D'_m = \left[a_l\left|V'_m\right| + D^*\right] \quad \text{(A.2)}$$

$$V'_m = -\frac{Q'(t)}{2\pi b\,\theta_m\, r} \quad \text{(A.3)}$$

$$\beta = \frac{\theta_{im} R_{im}}{\theta_m R_m} \quad \text{(A.4)}$$

where the symbols are defined by

$C'_m(r,t)$	solute concentration in the mobile region $[M/L^3]$
$C'_{im}(r,t)$	volume-averaged immobile region solute concentration $[M/L^3]$
$V'_m(r)$	mobile region seepage velocity [L/T]
D'_m	mobile region dispersion coefficient$[L^2/T]$
θ_m	mobile region porosity [unitless]
θ_{im}	immobile region porosity [unitless]
R_m	mobile region retardation factor [unitless]
R_{im}	immobile region retardation factor [unitless]
a_l	longitudinal dispersivity of the porous medium [L]
b	depth or thickness of aquifer region [L]
$Q'(t)$	extraction well pumping rate $[L^3/T]$
r	radial coordinate [L]

t	Time [T]
D^*	Molecular Diffusion Constant $[L^3/T]$

Therefore,

$$rD'_m = r\left[a_l\left|V'_m\right| + D^*\right] = r\left[a_l\frac{Q'(t)}{2\pi b\theta_m r} + D^*\right] = a_l\frac{Q'(t)}{2\pi b\theta_m} + rD^* \qquad \text{(A.5)}$$

So,

$$rD'_m\frac{\partial C'_m(r,t)}{\partial r} = \left(a_l\frac{Q'(t)}{2\pi b\theta_m} + rD^*\right)\frac{\partial C'_m(r,t)}{\partial r} \qquad \text{(A.6)}$$

The first term in equation (A.1) becomes

$$\frac{1}{R_m}\frac{1}{r}\frac{\partial}{\partial r}\left[\left(a_l\frac{Q'(t)}{2\pi b\theta_m} + rD^*\right)\frac{\partial C'_m(r,t)}{\partial r}\right] \qquad \text{(A.7)}$$

Applying the differentiation in equation (A.7) results in

$$\frac{1}{R_m}\frac{1}{r}\left[\left(a_l\frac{Q'(t)}{2\pi b\theta_m} + rD^*\right)\frac{\partial^2 C'_m(r,t)}{\partial^2 r} + D^*\frac{\partial C'_m(r,t)}{\partial r}\right] \qquad \text{(A.8)}$$

Rewriting the equation (A.8) and rearranging the transport equation (A.1) gives

$$\frac{\partial C'_m(r,t)}{\partial t} = \frac{1}{R_m}\left(\frac{a_l Q'(t)}{2\pi b\theta_m r} + D^*\right)\frac{\partial^2 C'_m(r,t)}{\partial^2 r} + \frac{1}{R_m}\left(\frac{Q'(t)}{2\pi b\theta_m r}\right)\frac{\partial C'_m(r,t)}{\partial r}$$
$$+\frac{1}{R_m}\frac{1}{r}\left(D^*\right)\frac{\partial C'_m(r,t)}{\partial r} - \frac{\theta_{im}R_{im}}{\theta_m R_m}\frac{\partial C'_{im}(r,t)}{\partial t} \qquad \text{where } r_w<r<\infty$$

(A.9)

In order to describe the transfer of solute between the mobile and immobile regions another equation is needed. A common model used is the first-order rate expression [Goltz & Oxley, 1991:548]:

$$\frac{\partial C'_{im}(r,t)}{\partial t} = \frac{\alpha'}{\theta_{im}R_{im}}\left[C'_m(r,t) - C'_{im}(r,t)\right] \qquad r_w < r < \infty \qquad \text{(A.10)}$$

where α' $[T^{-1}]$ is a first-order rate constant.

To create a dimensionless form of equation (A.10) the following variables and parameters are used

$$\beta = \frac{\theta_{im} R_{im}}{\theta_m R_m} \tag{A.11}$$

$$X = \frac{r}{a_1} \tag{A.12}$$

$$T = \frac{Q_{max}\, t}{2\pi b \theta_m a_1^2 R_m} \tag{A.13}$$

$$Q'(t) = Q_{max} Q(T) \tag{A.14}$$

$$C'_m(r,t) = C'_0 C_m(X,T) \text{ and } \quad C'_{im}(r,t) = C'_0 C_{im}(X,T) \tag{A.15}$$

where $C'_0 = \max\{C'_m(r,0)|r_w < r < \infty\} = \max\{C'_{im}(r,0)|r_w < r < \infty\}$ so,

$$\frac{\partial C'_m(r,t)}{\partial t} = C'_0 \frac{\partial C_m(X,T)}{\partial T}\frac{dT}{dt} = C'_0 \frac{Q_{max}}{2\pi b \theta_m a_1^2 R_m}\frac{\partial C_m(X,T)}{\partial T} \tag{A.16}$$

$$\frac{\partial C'_{im}(r,t)}{\partial t} = C'_0 \frac{Q_{max}}{2\pi b \theta_m a_1^2 R_m}\frac{\partial C_{im}(X,T)}{\partial T} \tag{A.17}$$

$$\frac{\partial C'_m(r,t)}{\partial r} = C'_0 \frac{\partial C_m(X,T)}{\partial X}\frac{\partial X}{\partial r} = \frac{C'_0}{a_1}\frac{\partial C_m(X,T)}{\partial X} \tag{A.18}$$

$$\frac{\partial^2 C_m(r,t)}{\partial r^2} = \frac{C'_0}{a_1^2}\frac{\partial^2 C_m(X,T)}{\partial X^2} \tag{A.19}$$

Plugging into the partial differential equation (A.9) yields

$$
\begin{aligned}
&C_0' \frac{Q_{max}}{2\pi b \theta_m a_l^2 R_m} \frac{\partial C_m(X,T)}{\partial T} = \frac{1}{R_m}\left(\frac{a_l Q_{max} Q(T)}{2\pi b \theta_m a_l X} + D^*\right)\frac{C_0'}{a_l^2}\frac{\partial^2 C_m(X,T)}{\partial X^2} \\
&+\frac{1}{R_m}\left(\frac{Q_{max} Q(T)}{2\pi b \theta_m a_l X}\right)\frac{C_0'}{a_l}\frac{\partial C_m(X,T)}{\partial X} + \frac{1}{R_m}\frac{1}{a_l X}\left(D^*\right)\frac{C_0'}{a_l}\frac{\partial C_m(X,T)}{\partial X} \\
&-\beta C_0' \frac{Q_{max}}{2\pi b \theta_m a_l^2 R_m}\frac{\partial C_{im}(X,T)}{\partial T}
\end{aligned}
\tag{A.20}
$$

Multiply both sides by:

$$
\frac{2\pi b \theta_m a_l^2 R_m}{C_0' Q_{max}} \tag{A.21}
$$

and canceling like terms results in,

$$
\begin{aligned}
&\frac{\partial C_m(X,T)}{\partial T} = \left(\frac{Q(T)}{X} + \frac{2\pi b \theta_m D^*}{Q_{max}}\right)\frac{\partial^2 C_m(X,T)}{\partial X^2} + \frac{Q(T)}{X}\frac{\partial C_m(X,T)}{\partial X} \\
&+\frac{2\pi b \theta_m}{Q_{max} X}\left(D^*\right)\frac{\partial C_m(X,T)}{\partial X} - \beta\frac{\partial C_{im}(X,T)}{\partial X}
\end{aligned}
\tag{A.22}
$$

Define $D = \dfrac{2\pi b \theta_m D^*}{Q_{max}}$ then equation (A.22) can be written as

$$
\frac{\partial C_m(X,T)}{\partial T} = \left(\frac{Q(T)}{X} + D\right)\frac{\partial^2 C_m(X,T)}{\partial X^2} + \left(\frac{Q(T)}{X} + \frac{D}{X}\right)\frac{\partial C_m(X,T)}{\partial X} - \beta\frac{\partial C_{im}(X,T)}{\partial X} \tag{A.23}
$$

Examining the second partial differential equation (A.10) and substituting in (A.11) - (A-15) in the equation

$$
\frac{\partial C_{im}'(r,t)}{\partial t} = \frac{\alpha'}{\theta_{im} R_{im}}\left[C_m'(r,t) - C_{im}'(r,t)\right] \tag{A.24}
$$

results in

$$C_0' \frac{Q_{max}}{2\pi b \theta_m a_l^2 R_m} \frac{\partial C_{im}(X,T)}{\partial T} = \frac{\alpha'}{\theta_{im} R_{im}} \left[C_o' C_m(X,T) - C_o' C_{im}(X,T) \right] \qquad \text{(A.25)}$$

Multiply equation (A.25) by

$$\frac{2\pi b \theta_m a_l^2 R_m}{C_0' Q_{max}} \qquad \text{(A.26)}$$

This results in,

$$\frac{\partial C_{im}(X,T)}{\partial T} = \frac{2\pi b a_l^2 \alpha'}{Q_{max} \beta} \left[C_m(X,T) - C_{im}(X,T) \right] \qquad \text{(A.27)}$$

Make the following substitution by defining the dimensionless first-order rate constant α as

$$\alpha = \frac{2\pi b a_l^2 \alpha'}{Q_{max} \beta} \qquad \text{(A.28)}$$

then equation (A.27) becomes

$$\frac{\partial C_{im}(X,T)}{\partial T} = \alpha \left[C_m(X,T) - C_{im}(X,T) \right] \qquad \text{(A.29)}$$

Now the groundwater transport is described in dimensionless form by the resulting two partial differential equations (A.29) and (A.30):

$$\frac{\partial C_m(X,T)}{\partial T} = \left(\frac{Q(T)}{X} + D \right) \frac{\partial^2 C_m(X,T)}{\partial X^2} + \left(\frac{Q(T)}{X} + \frac{D}{X} \right) \frac{\partial C_m(X,T)}{\partial X} - \beta \frac{\partial C_{im}(X,T)}{\partial X} \qquad \text{(A30)}$$

and

$$\frac{\partial C_{im}(X,T)}{\partial T} = \alpha \left[C_m(X,T) - C_{im}(X,T) \right] \qquad \text{(A.31)}$$

with the following initial conditions:

$$C_m(X,0) = \begin{cases} 1 & \text{for} \quad x_w < x < x_* \\ 0 & \text{for} \quad x_* < x < \infty \end{cases} \quad = \quad C_{m,o}(X) \tag{A.32}$$

and

$$C_{im}(X,0) = \begin{cases} 1 & \text{for} \quad x_w < x < x_* \\ 0 & \text{for} \quad x_* < x < \infty \end{cases} \quad = \quad C_{im,o}(X) \tag{A.33}$$

where X_* is some finite radius. Also the boundary conditions are written as

$$\frac{\partial C_m}{\partial X}(\infty,T) + C_m(\infty,T) = 0 \quad \text{and} \quad C_m(\infty,T) = 0 \quad \text{for} \quad \text{all} \quad 0 < T \leq T_3 \tag{A.34}$$

$$\frac{\partial C_{im}}{\partial X}(\infty,T) + C_{im}(\infty,T) = 0 \quad \text{and} \quad C_{im}(\infty,T) = 0 \quad \text{for} \quad \text{all} \quad 0 < T \leq T_3 \tag{A.35}$$

Appendix B

In this appendix a mathematical technique known as the Laplace transform is used to solve the initial boundary-value problems given in Appendix A. It converts initial-value problems involving linear differential equations as a function of time into an algebraic problem involving the Laplace transform variable (s) [Adams & Viramontes, 1993:3-12]. A general Laplace solution will be derived for the transport equation which is described as the dimensionless partial differential equation below (see equation A.30):

$$\frac{\partial C_m(X,T)}{\partial T} = \left(\frac{Q(T)}{X} + D\right)\frac{\partial^2 C_m(X,T)}{\partial X^2} + \left(\frac{Q(T)}{X} + \frac{D}{X}\right)\frac{\partial C_m(X,T)}{\partial X} - \beta\frac{\partial C_{im}(X,T)}{\partial T} \tag{B.1}$$

for $x_w < x < \infty$ and $0 < T < T_{final}$. If we suppose Q(T) = 1 for all T, we can apply the Laplace Transform technique. Let s denote the Laplace Transform variable.

$$\mathcal{L}\left(\frac{\partial C_m}{\partial T}\right) = \mathcal{L}\left[\left(\frac{1}{X} + D\right)\frac{\partial^2 C_m}{\partial X^2}\right] + \mathcal{L}\left[\left(\frac{1}{X} + \frac{D}{X}\right)\frac{\partial C_m}{\partial X}\right] - \mathcal{L}\left[\left(\beta\frac{\partial C_{im}}{\partial T}\right)\right] \tag{B.2}$$

Taking the Laplace Transform results in,

$$s\overline{C}_m - C_m(X,0) = \left(\frac{1}{X} + D\right)\frac{\partial^2 \overline{C}_m}{\partial X^2} + \left(\frac{1}{X} + \frac{D}{X}\right)\frac{\partial \overline{C}_m}{\partial X} - \beta\left[s\overline{C}_{im} - C_{im}(X,0)\right] \tag{B.3}$$

where

$\overline{C}_m(X,0)$ denotes the Laplace domain dimensionless mobile region solute concentration

$\overline{C}_{im}(X,s)$ denotes the Laplace domain volume-averaged immobile region solute concentration

s denotes the Laplace Transform variable

The second partial differential equation which describes the transfer of solute between the mobile and immobile regions (see equation A.31) after applying the Laplace transform becomes:

$$s\overline{C}_{im} - C_{im,0} = \alpha\left(\overline{C}_m - \overline{C}_{im}\right) \tag{B.4}$$

$$s\overline{C}_{im} - C_{im,0} = \alpha\,\overline{C}_m - \alpha\,\overline{C}_{im} \tag{B.5}$$

$$s\overline{C}_{im} + \alpha\,\overline{C}_{im} = \alpha\,\overline{C}_m + C_{im,0} \tag{B.6}$$

$$\overline{C}_{im} = \frac{\alpha\,\overline{C}_m + C_{im,0}}{s+\alpha} \tag{B.7}$$

Plugging equation (B.7) into equation (B.3) results in

$$s\overline{C}_m - C_{m,0} = \left(\frac{1}{X} + D\right)\frac{\partial^2 \overline{C}_m}{\partial X^2} + \left(\frac{1}{X} + \frac{D}{X}\right)\frac{\partial \overline{C}_m}{\partial X} - \beta\left[s\left(\frac{\alpha\,\overline{C}_m + C_{in,0}}{s+\alpha}\right) - C_{im,0}\right] \tag{B.8}$$

Expanding the third term on the right side yields

$$s\overline{C}_m - C_{m,0} = \left(\frac{1}{X} + D\right)\frac{\partial^2 \overline{C}_m}{\partial X^2} + \left(\frac{1}{X} + \frac{D}{X}\right)\frac{\partial \overline{C}_m}{\partial X} - \beta\left(\frac{s\alpha\,\overline{C}_m}{s+\alpha}\right) - \beta\left(\frac{sC_{im,0}}{s+\alpha}\right) + \beta C_{im,0} \tag{B.9}$$

Rearranging and collecting similar terms results in

$$\left(\frac{1}{X} + D\right)\frac{\partial^2 \overline{C}_m}{\partial X^2} + \left(\frac{1}{X} + \frac{D}{X}\right)\frac{\partial \overline{C}_m}{\partial X} - s\left(\frac{\beta\alpha}{s+\alpha} + 1\right)\overline{C}_m = -C_{m,0} - \beta\left(\frac{\alpha}{s+\alpha}\right)C_{im,0} \tag{B.10}$$

If we define

$$F(X)=\begin{cases}1 & x_w < x < x_* \\ 0 & x_* < x < \infty\end{cases} = C_{im}(X,0) = C_m(X,0) \qquad \text{(B.11)}$$

where F(X) is a dimensionless arbitrary initial concentration in both the mobile and the immobile region, then equation (B.10) becomes:

$$\left(\frac{1}{X}+D\right)\frac{\partial^2 \overline{C}_m}{\partial X^2}+\left(\frac{1}{X}+\frac{D}{X}\right)\frac{\partial \overline{C}_m}{\partial X}-s\left[\frac{\beta\alpha}{s+\alpha}+1\right]\overline{C}_m=-\left(\frac{\beta s}{s+\alpha}+1\right)F(X) \qquad \text{(B.12)}$$

If we let

$$\lambda=\left(\frac{\beta s}{s+\alpha}+1\right) \qquad \text{(B.13)}$$

and

$$\gamma=s\left(\frac{\beta\alpha}{s+\alpha}+1\right) \qquad \text{(B.14)}$$

then equation (B.12) reduces to:

$$\left(D+\frac{1}{X}\right)\frac{\partial^2 \overline{C}_m}{\partial X^2}+\left(\frac{D}{X}+\frac{1}{X}\right)\frac{\partial \overline{C}_m}{\partial X}-\gamma\,\overline{C}_m=\overline{F}(X,s) \qquad \text{(B.15)}$$

where $\overline{F}(X,s)=-\lambda\,F(X)$.

Appendix C

The Laplace transform equation, together with the appropriate initial and boundary conditions, including that molecular diffusion is negligible while mechanical dispersion dominates, results in a differential equation describing the extraction well when it is on in the form of:

$$\frac{1}{X}\frac{\partial^2 \overline{C}_m}{\partial X^2} + \frac{1}{X}\frac{\partial \overline{C}_m}{\partial X} - \gamma\,\overline{C}_m = \overline{F}(X,s) \qquad \text{(C.1)}$$

where the overbar indicates the Laplace transformation of the function. Multiplying through by X results in

$$\frac{\partial^2 \overline{C}_m}{\partial X^2} + \frac{\partial \overline{C}_m}{\partial X} - X\gamma\,\overline{C}_m = X\overline{F}(X,s) \qquad \text{(C.2)}$$

Assuming equation (C.2) has the following solution

$$\overline{C}_m(X,s) = \phi(X,s)e^{-\frac{1}{2}x} \qquad \text{(C.3)}$$

and substituting equation (C.3) into (C.2) yields

$$\frac{d^2\left(\phi e^{-\frac{1}{2}x}\right)}{dX^2} + \frac{d\left(\phi e^{-\frac{1}{2}x}\right)}{dX} - X\gamma\left[\phi e^{-\frac{1}{2}x}\right] = X\overline{F}(X,s) \qquad \text{(C.4)}$$

Differentiating the first term of equation (C.4) results in

$$\frac{d}{dX}\left(\frac{d\,\phi e^{-\frac{1}{2}x}}{dX}\right) = e^{-\frac{1}{2}x}\frac{d^2\phi}{dX^2} - e^{-\frac{1}{2}x}\frac{d\phi}{dX} + \frac{1}{4}\phi e^{-\frac{1}{2}x} \qquad \text{(C.5)}$$

Evaluating the second term of equation (C.5) results in

$$\frac{d}{dX}\left(\phi e^{-\frac{1}{2}x}\right) = -\frac{1}{2}\phi\left(e^{-\frac{1}{2}x}\right) + e^{-\frac{1}{2}x}\frac{d\phi}{dX} \qquad \text{(C.6)}$$

Combining both terms, simplifying, and inserting back into equation (C.4) gives

$$e^{-\frac{1}{2}X}\frac{d^2\phi}{dX^2}-\frac{1}{4}\phi e^{-\frac{1}{2}X}-X\gamma\phi e^{-\frac{1}{2}X}=X\overline{F}(X,s) \tag{C.7}$$

Multiplying each term by $e^{\frac{1}{2}X}$ gives

$$\frac{d^2\phi}{dx^2}-\gamma\left[X+\frac{1}{4\gamma}\right]\phi=e^{\frac{1}{2}x}X\overline{F}(X,s) \tag{C.8}$$

Employing the change of variables $y=\gamma^{\frac{1}{3}}\left[X+\frac{1}{4\gamma}\right]$, and $\Phi(y,s)=\phi(X,s)$ leads to the following equation

$$\frac{d^2\Phi}{dy^2}-y\Phi=\gamma^{-\frac{2}{3}}\exp\left(\frac{1}{2}\left[\gamma^{-\frac{1}{3}}y-4\gamma^{-1}\right]\right)\overline{F}(\gamma^{\frac{1}{3}}y-4\gamma^{-1},s)\equiv\mathfrak{I}(y,s) \qquad y_w<y<\infty \tag{C.9}$$

See (Adams & Viramontes, 1993) pages A-64 through A-65 for derivation and rationale for variable change. The boundary conditions, change also, again see (Adams & Viramontes, 1993) pages A-65 through A-68 for rationale and derivation to become,

$$-\frac{1}{2}\Phi(y_w)+\gamma^{\frac{1}{3}}\frac{d\Phi(y_w)}{dy}=0 \tag{C.10}$$

$$\frac{1}{2}\Phi(\infty)+\gamma^{\frac{1}{3}}\frac{d\Phi(\infty)}{dy}=0 \tag{C.11}$$

The general solution to equation (C.9) is of the form

$$\Phi(y) = C_1\,\Phi_1(y) + C_1\,\Phi_2 + \Phi_p \tag{C.12}$$

where C_1 and C_2 are constants, and $\Phi_1(y)$ and $\Phi_2(y)$ are the complementary solutions. and Φ_p is the particular solution. Also, $\Phi_1(y)$ and $\Phi_2(y)$ satisfy the boundary conditions (C.10) and (C.11), respectively, so that

$$\Phi_1(y) = A\,Ai(y) + BBi(y) \tag{C.13}$$

$$\Phi_2(y) = CAi(y) + DBi(y) \tag{C.14}$$

where A, B, C, and D are constants and Ai(y) and Bi(y) are Airy and Bairy functions, respectively (Abramowitz and Stegun, 1970). Equation (C.9) has the solution in the form

$$\Phi(y,s) = \int_{y_w}^{\infty} g(y,\eta,s)\mathcal{I}(\eta,s)\,d\,\eta \tag{C.15}$$

where $g(y,\eta,s)$ is the Green's function given by:

$$g(y,\eta,s) = \begin{cases} \dfrac{\Phi_1(y)\Phi_2(\eta)}{W[\Phi_1,\Phi_2](\eta)} & y < \eta < \infty \\ \dfrac{\Phi_1(\eta)\Phi_2(y)}{W[\Phi_1,\Phi_2](\eta)} & y_w \le \eta \le y \end{cases} \tag{C.16}$$

where $W[\Phi_1,\Phi_2](\eta)$ is the Wronskian of Φ_1 and Φ_2.

To find the solution to $\Phi_1(y)$ we apply the boundary condition at y_w, which is

$$-\frac{1}{2}\Phi(y_w) + \gamma^{\frac{1}{3}}\frac{d\,\Phi(y_w)}{dy} = 0 \tag{C.17}$$

Solving for Φ_1 and applying the boundary conditions at y_w yields:

$$\Phi_1(y) = A\left[Ai(y) - \frac{G[Ai]}{G[Bi]}Bi(y)\right] \tag{C.18}$$

where

$$G[Ai] = -\frac{1}{2}Ai(y_w) + \gamma^{\frac{1}{3}}\frac{dAi}{dy}(y_w) \tag{C.19}$$

and

$$G[Bi] = -\frac{1}{2}Bi(y_w) + \gamma^{\frac{1}{3}}\frac{dBi}{dy}(y_w) \tag{C.20}$$

To find the solution to $\Phi_2(y)$ we apply the boundary conditions at $y = \infty$ which yields:

$$\Phi_2(y) = CAi(y) \tag{C.21}$$

that is, D = 0. To find the particular solution to equation (C.9) and construct the Green's function equation (C.16) we need to determine the Wronskian

$$W[\Phi_1, \Phi_2](y) = \begin{vmatrix} \Phi_1 & \Phi_2 \\ \Phi_1' & \Phi_2' \end{vmatrix} \tag{C.22}$$

So equation (C.22) becomes

$$W[\Phi_1, \Phi_2](y) = \begin{vmatrix} A\left[A_i(y) - \frac{G[Ai]}{G[Bi]}B_i(y)\right] & C[Ai(y)] \\ A\left[A'i(y) - \frac{G[Ai]}{G[Bi](y_w)}B_i'(y)\right] & C[A'i(y)] \end{vmatrix} \tag{C.23}$$

Simplifying equation (C.23) becomes

$$W[\Phi_1,\Phi_2](y) = AC\left\{Ai(y)B'i(y)\frac{G[A_i]}{G[B_i]} - A'i(y)Bi(y)\frac{G[A_i]}{G[B_i]}\right\} \tag{C.24}$$

or
$$W[\Phi_1,\Phi_2](y) = AC\left[\frac{G[Ai](y_w)}{G[Bi](y_w)}\right]W[Ai,Bi](y) \tag{C.25}$$

since the Airy function approaches zero as its argument approaches infinity.

Knowing $W[Ai,Bi](y) = \frac{1}{\pi}$ (see Abramowitz and Stegun, 1970) equation (C.25) becomes:

$$W[\Phi_1,\Phi_2](y) = AC\left[\frac{G[Ai]}{G[Bi]}\right]\frac{1}{\pi} \tag{C.26}$$

that is, the Wronskian is a constant. Substituting this into equation (C.16) the Green's function becomes:

$$g(y,\eta) = \begin{cases} \dfrac{A\left[Ai(y) - \dfrac{G[Ai]}{G[Bi]}Bi(y)\right]CAi(\eta)}{AC\left[\dfrac{G[Ai]}{G[Bi]}\right]\dfrac{1}{\pi}} & y < \eta < \infty \\[2ex] \dfrac{A\left[Ai(\eta) - \dfrac{G[Ai]}{G[Bi]}Bi(\eta)\right]CAi(y)}{AC\left[\dfrac{G[Ai]}{G[Bi]}\right]\dfrac{1}{\pi}} & y_w \le \eta \le y \end{cases} \tag{C.27}$$

Simplifying the Green's function becomes:

$$g(y,\eta,s)=\begin{cases}\pi\left[\mathrm{Ai}(y)\dfrac{G[\mathrm{Bi}]}{G[\mathrm{Ai}]}-\mathrm{Bi}(y)\right]\mathrm{Ai}(\eta) & y<\eta<\infty \\ \pi\left[\mathrm{Ai}(\eta)\dfrac{G[\mathrm{Bi}]}{G[\mathrm{Ai}]}-\mathrm{Bi}(\eta)\right]\mathrm{Ai}(y) & y_w\le\eta\le y\end{cases} \tag{C.28}$$

Through a manipulation of variables $\overline{C}_m(X,s)$ becomes,

$$\overline{C}_m(X,s)=e^{-\frac{1}{2}x}\int_{x_w}^{\infty}\mathfrak{g}(x,\xi,s)\gamma^{-\frac{1}{3}}e^{\frac{1}{2}\xi}\,\overline{F}(\xi,s)\,d\xi \tag{C.29}$$

(see Adams & Viramontes, 1993) pages A-77 through A-78 for a more thorough derivation and explanation.

Verifying the nonhomogeneous boundary value problem:

$$\Phi(y)=C_1\,\Phi_1(y)+C_1\,\Phi_2+\Phi_p \tag{C.30}$$

together with the boundary conditions

$$\Phi_1(y)=\mathrm{AAi}(y)+\mathrm{BBi}(y) \tag{C.31}$$

$$\Phi_2(y)=\mathrm{C\,Ai}(y)+\mathrm{DBi}(y) \tag{C.32}$$

has the unique solution

$$\begin{aligned}\Phi(y,s)&=\pi\int_{y_w}^{y}\left[\mathrm{Ai}(\eta)\frac{G[\mathrm{Bi}]}{G[\mathrm{Ai}]}\mathrm{Ai}(y)-\mathrm{Bi}(\eta)\,\mathrm{Ai}(y)\right]\mathfrak{I}(\eta,s)\,d\eta\\&+\pi\int_{y}^{\infty}\left[\mathrm{Ai}(y)\frac{G[\mathrm{Bi}]}{G[\mathrm{Ai}]}\mathrm{Ai}(\eta)-\mathrm{Bi}(y)\,\mathrm{Ai}(\eta)\right]\mathfrak{I}(\eta,s)\,d\eta\end{aligned} \tag{C.33}$$

Expanding equation (C.33) results in:

$$\Phi(y,s)=\pi\frac{G[Bi]}{G[Ai]}Ai(y)\int_{y_w}^{y}Ai(\eta)\mathfrak{I}(\eta,s)\,d\eta-\pi\,Ai(y)\int_{y_w}^{y}Bi(\eta)\mathfrak{I}(\eta,s)\,d\eta$$
$$+\pi\frac{G[Bi]}{G[Ai]}Ai(y)\int_{y}^{\infty}Ai(\eta)\mathfrak{I}(\eta,s)\,d\eta-\pi\,Bi(y)\int_{y}^{\infty}Ai(\eta)\mathfrak{I}(\eta,s)\,d\eta \tag{C.34}$$

Combining equation (C.29) and (C.34) results in the solution

$$\overline{C}_m(X,s)=\pi e^{-\frac{1}{2}x}\gamma^{-\frac{1}{3}}\left\{\begin{array}{l}\frac{G[Bi]}{G[Ai]}Ai\left[\gamma^{\frac{1}{3}}\left(X+\frac{1}{4\gamma}\right)\right]\int_{x_w}^{x}Ai\left[\gamma^{\frac{1}{3}}\left(\xi+\frac{1}{4\gamma}\right)\right]e^{\frac{1}{2}\xi}\,\overline{F}(\xi,s)\,d\xi\\ -Ai\left[\gamma^{\frac{1}{3}}\left(X+\frac{1}{4\gamma}\right)\right]\int_{x_w}^{x}Bi\left[\gamma^{\frac{1}{3}}\left(\xi+\frac{1}{4\gamma}\right)\right]e^{\frac{1}{2}\xi}\,\overline{F}(\xi,s)\,d\xi\\ +\frac{G[Bi]}{G[Ai]}Ai\left[\gamma^{\frac{1}{3}}\left(X+\frac{1}{4\gamma}\right)\right]\int_{x}^{\infty}Ai\left[\gamma^{\frac{1}{3}}\left(\xi+\frac{1}{4\gamma}\right)\right]e^{\frac{1}{2}\xi}\,\overline{F}(\xi,s)\,d\xi\\ -Bi\left[\gamma^{\frac{1}{3}}\left(X+\frac{1}{4\gamma}\right)\right]\int_{x}^{\infty}Ai\left[\gamma^{\frac{1}{3}}\left(\xi+\frac{1}{4\gamma}\right)\right]e^{\frac{1}{2}\xi}\,\overline{F}(\xi,s)\,d\xi\end{array}\right\} \tag{C.35}$$

Solving for $\overline{C}_m(X_w,s)$ at the well results in the following equation where the first and second term in equation (C.35) are zero at the well.

$$\overline{C}_m(X_w,s)=\pi e^{-\frac{1}{2}x}\gamma^{-\frac{1}{3}}\left[\frac{G[Bi]}{G[Ai]}Ai(y_w)-Bi(y_w)\right]\int_{x_w}^{\infty}Ai\left[\gamma^{\frac{1}{3}}\left(\xi+\frac{1}{4\gamma}\right)\right]e^{\frac{1}{2}\xi}\,\overline{F}(\xi,s)\,d\xi \tag{C.36}$$

$$=\frac{\pi e^{-\frac{1}{2}x}\gamma^{-\frac{1}{3}}}{G[Ai]}\left[G[Bi]Ai(y_w)-G[Ai]Bi(y_w)\right]\int_{x_w}^{\infty}Ai\left[\gamma^{\frac{1}{3}}\left(\xi+\frac{1}{4\gamma}\right)\right]e^{\frac{1}{2}\xi}\,\overline{F}(\xi,s)\,d\xi \tag{C.37}$$

$$=\frac{\pi e^{-\frac{1}{2}x}\gamma^{-\frac{1}{3}}}{G[Ai]}\left[\left[-\frac{1}{2}Bi(y_w)+\gamma^{\frac{1}{3}}B'i(y_w)\right]Ai(y_w)-\left[-\frac{1}{2}Ai(y_w)+\gamma^{\frac{1}{3}}A'i(y_w)\right]Bi(y_w)\right]$$
$$\times\int_{x_w}^{\infty}Ai\left[\gamma^{\frac{1}{3}}\left(\xi+\frac{1}{4\gamma}\right)\right]e^{\frac{1}{2}\xi}\,\overline{F}(\xi,s)\,d\xi \tag{C.38}$$

$$= \frac{\pi e^{-\frac{1}{2}x}}{G[Ai]}\left[\left(Ai(y_w)B'i(y_w)_i - A'i(y_w)Bi(y_w)\right)\right]\int_{x_w}^{\infty} Ai\left[\gamma^{\frac{1}{3}}\left(\xi + \frac{1}{4\gamma}\right)\right]e^{\frac{1}{2}\xi}\,\overline{F}(\xi,s)\,d\xi \qquad (C.39)$$

noting that $\left(Ai(y_w)B'i(y_w) - A'i(y_w)Bi(y_w)\right) = W[Ai,Bi](y_w) = \frac{1}{\pi}$ yields the following solution to $\overline{C}_m(X_w,s)$ in the Laplace domain:

$$\overline{C}_m(X_w,s) = \frac{e^{-\frac{1}{2}x}}{G[Ai]}\int_{x_w}^{\infty} Ai\left[\gamma^{\frac{1}{3}}\left(\xi + \frac{1}{4\gamma}\right)\right]e^{\frac{1}{2}\xi}\,\overline{F}(\xi,s)\,d\xi \qquad (C.40)$$

Appendix D

In this appendix, the Laplace transform equation together with the appropriate initial and boundary conditions, including that mechanical dispersion is negligible while molecular diffusion dominates, results in a differential equation describing the extraction well when it is off in the form of:

$$D\frac{\partial^2 \overline{C}_m}{\partial X^2}+\frac{D}{X}\frac{\partial \overline{C}_m}{\partial X}-\gamma\,\overline{C}_m=\overline{F}(X,s) \tag{D.1}$$

Where the overbar indicates the Laplace Transform of the function.

Multiplying through by X/D results in:

$$X\frac{\partial^2 \overline{C}_m}{\partial X^2}+\frac{\partial \overline{C}_m}{\partial X}-\frac{X}{D}\gamma\,\overline{C}_m=\frac{X}{D}\overline{F}(X,s)=X\mathfrak{I}(X,s) \tag{D.2}$$

This results in the differential equation

$$X\frac{\partial^2 \overline{C}_m}{\partial X^2}+\frac{\partial \overline{C}_m}{\partial X}-X\tilde{\gamma}\,\overline{C}_m=X\mathfrak{I}(X,s) \tag{D.3}$$

where

$$\tilde{\gamma}=\frac{1}{D}\gamma \tag{D.4}$$

The boundary conditions associated with this differential equation are obtained by taking the Laplace Transform of the corresponding boundary conditions.

$$\mathcal{L}\left(\frac{\partial C_m}{\partial X}(X_w,T)\right)=0 \tag{D.5}$$

yields

$$\frac{\partial \overline{C}_m}{\partial X}(X_w, s) = 0 \qquad \text{(D.6)}$$

and

$$\mathcal{L}\left(\frac{\partial C_m}{\partial X}(\infty, T) + C_m(\infty, T)\right) = 0 \qquad \text{(D.7)}$$

yields

$$\frac{\partial \overline{C}_m}{\partial X}(\infty, s) + \overline{C}_m(\infty, s) = 0 \qquad \text{(D.8)}$$

Assuming equation (D.1) has a solution of the form

$$\overline{C}_m(X, s) = \phi(X, s) \qquad \text{(D.9)}$$

that satisfies the differential equation (D.1) and the boundary conditions (equations D.6 and (D.8) then substituting into equation (D.3) yields:

$$X\frac{d^2\phi(X,s)}{dX^2} + \frac{d\phi(X,s)}{dX} - \tilde{\gamma}\, X\phi(X,s) = X\Im(X,s) \qquad \text{(D.10)}$$

In order to construct the Green's function, we seek a simpler equation where the left-hand side has no constant in the third term. Therefore, define y = AX where A is a constant to be determined and

$$\Phi(y, s) = \phi(X, s) \qquad \text{(D.11)}$$

then equation (D.10) becomes

$$XA^2\frac{d^2\Phi(y,s)}{dy^2} + A\frac{d\Phi(y,s)}{dy} - \tilde{\gamma}\, X\Phi(y,s) = X\Im(\frac{y}{A}, s) \qquad \text{(D.12)}$$

Multiplying through by X gives:

$$X^2 A^2 \frac{d^2 \Phi(y,s)}{d y^2} + AX \frac{d\Phi(y,s)}{d y} - \tilde{\gamma} X^2 \Phi(y,s) = X^2 \mathfrak{I}(\frac{y}{A}, s) \tag{D.13}$$

or

$$y^2 \frac{d^2 \Phi(y,s)}{dy^2} + y \frac{d\Phi(y,s)}{dy} - \frac{\tilde{\gamma} y^2}{A^2} \Phi(y,s) = \frac{y^2}{A^2} \mathfrak{I}(\frac{y}{A}, s) \tag{D.14}$$

If we choose A such that

$$\frac{\tilde{\gamma}}{A^2} = 1 \tag{D.15}$$

$$A = \tilde{\gamma}^{\frac{1}{2}} \tag{D.16}$$

then

$$y = \tilde{\gamma}^{\frac{1}{2}} X \tag{D.17}$$

Dividing equation (D.14) by y^2 yields the following equation:

$$\frac{d^2 \Phi(y,s)}{dy^2} + \frac{1}{y} \frac{d\Phi(y,s)}{dy} - \Phi(y,s) = \frac{1}{\tilde{\gamma}} \mathfrak{I}(\frac{y}{\tilde{\gamma}^{\frac{1}{2}}}, s) \equiv \mathfrak{I}^*(y,s) \tag{D.18}$$

on the interval $y_w < y < \infty$.

Looking at the Laplace transformed boundary condition at the dimensionless well radius (equation D.5) and converting it into terms of y_w yields:

$$\frac{d\Phi}{dy}(y_w, s) = 0 \tag{D.19}$$

where

$$y_w = \tilde{\gamma}^{\frac{1}{2}} X_w \tag{D.20}$$

Looking at the boundary condition at infinity, and rewriting in terms of $y = \infty$ yields

$$\tilde{\gamma}^{\frac{1}{2}} \frac{d\Phi}{dy}(\infty, s) + \Phi(\infty, s) = 0 \qquad \text{(D.21)}$$

since

$$y = \tilde{\gamma}^{\frac{1}{2}} X \qquad \text{(D.22)}$$

then $y \to \infty$ as $X \to \infty$.

To derive the Green's Function associated with this boundary-value problem, we first find the general solution to the homogeneous problem. That is, we seek the complementary solution to equation (D.18):

$$\frac{d^2\Phi(y,s)}{dy^2} + \frac{1}{y}\frac{d\Phi(y,s)}{dy} - \Phi(y,s) = 0 \qquad y_w < y < \infty \qquad \text{(D.23)}$$

Solutions are in the form of the modified Bessel functions of order zero [Abramowitz & Stegun, 1970]. The general solution of this homogeneous differential equation is of the form:

$$\Phi(y,s) = C_1\,\Phi_1(y,s) + C_2\,\Phi_2(y,s) \qquad \text{(D.24)}$$

where C_1 and C_2 are constants and $\Phi_1(y,s)$ satisfies the differential equation and the boundary condition at $y = y_w$ and $\Phi_2(y,s)$ satisfies the differential equation and the boundary condition at $y = \infty$. Both of the solutions are of the form:

$$\Phi_1(y,s) = AI_o(y) + BK_o(y) \qquad \text{(D.25)}$$

and

$$\Phi_2(y,s) = CI_o(y) + DK_o(y) \qquad \text{(D.26}$$

Here A,B,C, and D are constants dependent on s to be determined and $I_o(y)$ and $K_o(y)$ are Bessel functions of the first kind, order zero and third kind, order zero, respectively.

To find a solution, $\Phi_1(y,s)$, we apply the boundary condition at the well (equation D.19):

$$\frac{d\Phi_1}{dy}(y_w) = 0 = AI_o'(y_w) + BK_o'(y_w) \tag{D.27}$$

thus

$$A = \frac{-BK_o'(y_w)}{I_o'(y_w)} \tag{D.28}$$

so,

$$\Phi_1(y,s) = B\left[\frac{-K_o'(y_w)}{I_o'(y_w)} I_o(y) + K_o(y)\right] \tag{D.29}$$

If we choose $B = I_o'(y_w)$, then equation (D.29) becomes:

$$\Phi_1(y,s) = -K_o'(y_w) I_o(y) + I_o'(y_w) K_o(y) \qquad \text{(D.30}$$

To find a solution, $\Phi_2(y,s)$ we apply the boundary condition at $y = \infty$ (equation D.21)

$$\tilde{\gamma}^{\frac{1}{2}} \frac{d\Phi_2}{dy}(\infty, s) - \Phi_2(\infty, s) = 0 \tag{D.31}$$

Thus

$$\tilde{\gamma}^{\frac{1}{2}} \frac{d\Phi}{dy}\left[CI_o'(\infty,s) + DK_o'(\infty,s)\right] + CI_o(\infty,s) + DK_o(\infty,s) = 0 \tag{D.32}$$

or

$$C\left[\tilde{\gamma}^{\frac{1}{2}} I_o'(\infty,s)+I_o(\infty,s)\right]+D\left[\tilde{\gamma}^{\frac{1}{2}} K_o'(\infty,s)+K_o(\infty,s)\right]=0 \tag{D.33}$$

But this is only true if C is chosen to be zero. Hence,

$$\Phi_2(y,s)=DK_o(y) \tag{D.34}$$

Without loss of generality, we can take D=1.

We now seek the particular solution to equation (D.10) using a Green's function which is of the form:

$$g(y,\eta,s)=\begin{cases}\dfrac{\Phi_1(y)\Phi_2(\eta)}{W[\Phi_1,\Phi_2](\eta)} & y<\eta<\infty \\ \dfrac{\Phi_1(\eta)\Phi_2(y)}{W[\Phi_1,\Phi_2](\eta)} & y_w\le\eta\le y\end{cases} \tag{D.35}$$

where $W[\Phi_1,\Phi_2](\eta)$ is the Wronskian of Φ_1 and Φ_2. Determining the Wronskian

$$W[\Phi_1,\Phi_2](y)=\begin{vmatrix}\Phi_1 & \Phi_2\\ \Phi_1' & \Phi_2'\end{vmatrix} \tag{D.36}$$

so,

$$W[\Phi_1,\Phi_2](y)=\begin{vmatrix}-K_o'(y_w)I_o(y)+I_o'(y_w)K_o(y) & K_o(y)\\ -K_o'(y_w)I_o'(y)+I_o'(y_w)K_o'(y) & K_o'(y)\end{vmatrix} \tag{D.37}$$

$$=\left[-K_o'(y_w)I_o(y)+I_o'(y_w)K_o(y)\right]K_o'(y)-\left[-K_o'(y_w)I_o'(y)+I_o'(y_w)K_o'(y)\right]K_o(y) \tag{D.38}$$

$$=K_o'(y_w)\left[K_o(y_w)I_o'(y)-K_o'(y)I_o(y_w)\right] \tag{D.39}$$

$$= K_o'(y_w) W[K_o, I_o](y) \tag{D.40}$$

where $$W[K_o, I_o](y) = \frac{1}{y} \tag{D.41}$$

so, $$W[\Phi_1, \Phi_2](y) = \frac{1}{y} K_o'(y_w) \tag{D.42}$$

Thus the Green's function

$$g(y,\eta) = \begin{cases} \dfrac{\Phi_1(y)\Phi_2(\eta)}{W[\Phi_1,\Phi_2](\eta)} & y < \eta < \infty \\ \dfrac{\Phi_1(\eta)\Phi_2(y)}{W[\Phi_1,\Phi_2](\eta)} & y_w \le \eta \le y \end{cases} \tag{D.43}$$

becomes

$$g(y,\eta,s) = \begin{cases} \dfrac{\eta[I_o'(y_w)K_o(y) - K_o'(y_w)I_o(y)]K_o(\eta)}{K_o'(y_w)} & y < \eta < \infty \\ \dfrac{\eta[I_o'(y_w)K_o(\eta) - K_o'(y_w)I_o(\eta)]K_o(y)}{K_o'(y_w)} & y_w \le \eta \le y \end{cases} \tag{D.44}$$

The general solution to equation (D.18) is of the form

$$\Phi(y) = \int_{y_w}^{\infty} g(y,\eta,s)\mathcal{F}^*(\eta,s)\,d\eta \tag{D.45}$$

Since $y = \tilde{\gamma}^{\frac{1}{2}} X$, then $\eta = \tilde{\gamma}^{\frac{1}{2}}\xi$ and $d\eta = \tilde{\gamma}^{\frac{1}{2}} d\xi$, then equation (D.45), together with the right hand side of equation (D.18) becomes

$$\Phi(y,s) = \int_{X_w}^{\infty} g\left(\tilde{\gamma}^{\frac{1}{2}} X, \tilde{\gamma}^{\frac{1}{2}}\xi, s\right)\mathcal{F}^*\left(\tilde{\gamma}^{\frac{1}{2}}\xi, s\right)\tilde{\gamma}^{\frac{1}{2}}\,d\xi \tag{D.46}$$

$$= \int_{X_w}^{\infty} g\left(\tilde{\gamma}^{\frac{1}{2}} X, \tilde{\gamma}^{\frac{1}{2}}\xi, s\right)\tilde{\gamma}^{-\frac{1}{2}}\,\overline{F}(\xi,s)\tilde{\gamma}^{\frac{1}{2}}\,d\xi \tag{D.47}$$

Since $\overline{C}_m(X,s) = \phi(X,s)$ and $\Phi(y,s) = \phi(X,s)$ then

$$\overline{C}_m(X,s)=\int_{X_w}^{\infty} g\left(\tilde{\gamma}^{\frac{1}{2}}X,\tilde{\gamma}^{\frac{1}{2}}\xi,s\right)\overline{F}(\xi,s)\,d\xi \tag{D.48}$$

If we define
$$\mathfrak{h}(X,\xi,s)=g\left(\tilde{\gamma}^{\frac{1}{2}}X,\tilde{\gamma}^{\frac{1}{2}}\xi,s\right) \tag{D.49}$$

then

$$\overline{C}_m(X,s)=\int_{X_w}^{\infty}\mathfrak{h}(X,\xi,s)\,\overline{F}(\xi,s)\,d\xi \tag{D.50}$$

Substituting in the constructed Green's functions (equation D.44) using equation (D.18) yields

$$\begin{aligned}\Phi(y)=&\int_{y_w}^{y}\eta\left[\frac{\left[I_o'(y_w)K_o(\eta)-K_o'(y_w)I_o(\eta)\right]}{K_o'(y_w)}\right]K_o(y)\mathcal{F}^*(\eta,s)\,d\eta\\&+\int_{y}^{\infty}\eta\left[\frac{\left[I_o'(y_w)K_o(y)-K_o'(y_w)I_o(y)\right]}{K_o'(y_w)}\right]K_o(\eta)\mathcal{F}^*(\eta,s)\,d\eta\end{aligned} \tag{D.51}$$

Combining terms

$$\begin{aligned}\Phi(y)=&\frac{I_o'(y_w)}{K_o'(y_w)}K_o(y)\int_{y_w}^{y}\eta K_o(\eta)\mathcal{F}^*(\eta,s)\,d\eta-K_o(y)\int_{y_w}^{y}\eta I_o(\eta)\mathcal{F}^*(\eta,s)\,d\eta\\&+\frac{I_o'(y_w)}{K_o'(y_w)}K_o(y)\int_{y}^{\infty}\eta K_o(\eta)\mathcal{F}^*(\eta,s)\,d\eta-I_o(y)\int_{y}^{\infty}\eta K_o(\eta)\mathcal{F}^*(\eta,s)\,d\eta\end{aligned} \tag{D.52}$$

Therefore,

$$\overline{C}_m(X,s)=\begin{bmatrix}\dfrac{I_o'(y_w)}{K_o'(y_w)}K_o\left(\tilde{\gamma}^{\frac{1}{2}}X\right)\int_{X_w}^{\infty}\xi K_o\left(\tilde{\gamma}^{\frac{1}{2}}\xi\right)\overline{F}(\xi,s)\,d\xi\\-K_o\left(\tilde{\gamma}^{\frac{1}{2}}X\right)\int_{X_w}^{X}\xi I_o\left(\tilde{\gamma}^{\frac{1}{2}}\xi\right)\overline{F}(\xi,s)\,d\xi\\-I_o\left(\tilde{\gamma}^{\frac{1}{2}}X\right)\int_{X_w}^{\infty}\xi K_o\left(\tilde{\gamma}^{\frac{1}{2}}\xi\right)\overline{F}(\xi,s)\,d\xi\end{bmatrix} \tag{D.53}$$

Solving for $\overline{C}_m(X_w,s)$ at the well results in the following equation where the second term in equation (D.53) is zero at the well.

$$\overline{C}_m(X_w,s) = \frac{I_o'\left(\tilde{\gamma}^{\frac{1}{2}} X_w\right) K_o\left(\tilde{\gamma}^{\frac{1}{2}} X_w\right)}{K_o'\left(\tilde{\gamma}^{\frac{1}{2}} X_w\right)} \int_{X_w}^{\infty} \xi K_o\left(\tilde{\gamma}^{\frac{1}{2}}\xi\right) \overline{F}(\xi,s)\, d\xi - I_o\left(\tilde{\gamma}^{\frac{1}{2}} X_w\right) \int_{X_w}^{\infty} \xi K_o\left(\tilde{\gamma}^{\frac{1}{2}}\xi\right) \overline{F}(\xi,s)\, d\xi \tag{D.54}$$

Simplifying

$$\overline{C}_m(X_w,s) = \frac{\tilde{\gamma}}{K_o'\left(\tilde{\gamma}^{\frac{1}{2}} X_w\right)} \left[I_o'\left(\tilde{\gamma}^{\frac{1}{2}} X_w\right) K_o\left(\tilde{\gamma}^{\frac{1}{2}} X_w\right) - I_o\left(\tilde{\gamma}^{\frac{1}{2}} X_w\right) K_o'\left(\tilde{\gamma}^{\frac{1}{2}} X_w\right) \right] \int_{X_w}^{\infty} \xi K_o\left(\tilde{\gamma}^{\frac{1}{2}}\xi\right) \overline{F}(\xi,s)\, d\xi \tag{D.55}$$

Noting that

$$\begin{aligned} W[K_o, I_o]\left(\tilde{\gamma}^{\frac{1}{2}} X_w\right) &= I_o'\left(\tilde{\gamma}^{\frac{1}{2}} X_w\right) K_o\left(\tilde{\gamma}^{\frac{1}{2}} X_w\right) - I_o\left(\tilde{\gamma}^{\frac{1}{2}} X_w\right) K_o'\left(\tilde{\gamma}^{\frac{1}{2}} X_w\right) \\ &= \frac{1}{\tilde{\gamma}^{\frac{1}{2}} X_w} \end{aligned} \tag{D.56}$$

then equation (D.55) becomes,

$$\overline{C}_m(X_w,s) = \frac{\tilde{\gamma}}{K_o'\left(\tilde{\gamma}^{\frac{1}{2}} X_w\right)} W[K_o, I_o]\left(\tilde{\gamma}^{\frac{1}{2}} X_w\right) \int_{X_w}^{\infty} \xi K_o\left(\tilde{\gamma}^{\frac{1}{2}}\xi\right) \overline{F}(\xi,s)\, d\xi \tag{D.57}$$

This yields the following solution to $\overline{C}_m(X_w, s)$ in the Laplace domain:

$$\overline{C}_m(X_w,s) = \frac{\tilde{\gamma}^{\frac{1}{2}}}{X_w K_o'\left(\tilde{\gamma}^{\frac{1}{2}} X_w\right)} \int_{X_w}^{\infty} \xi K_o\left(\tilde{\gamma}^{\frac{1}{2}}\xi\right) \overline{F}(\xi,s)\, d\xi \tag{D.58}$$

Appendix E

In this appendix, we will recall the partial differential equations (A.30) and (A.31) formed earlier in dimensionless form,

$$\frac{\partial C_m(X,T)}{\partial T}=\left(\frac{Q(T)}{X}+D\right)\frac{\partial^2 C_m(X,T)}{\partial X^2}+\left(\frac{Q(T)}{X}+\frac{D}{X}\right)\frac{\partial C_m(X,T)}{\partial X}-\beta\frac{\partial C_{im}(X,T)}{\partial T} \qquad \text{(E.1)}$$

and

$$\frac{\partial C_{im}(X,T)}{\partial T}=\alpha\left[C_m(X,T)-C_{im}(X,T)\right] \qquad \text{(E.2)}$$

Multiplying equation (E.2) by the integration factor $\mu(T)=e^{\alpha T}$ yields

$$\frac{\partial}{\partial T}\left[e^{\alpha T}C_{im}(X,T)\right]=\alpha e^{\alpha T}C_m(X,T) \qquad \text{(E.3)}$$

Integrating both sides of equation (E.3) with respect to time T and evaluating results in

$$e^{\alpha T}C_{im}(X,T)-e^{\alpha * 0}C_{im,0}(X,0)=\alpha\int_0^T e^{\alpha\tau}C_m(X,\tau)\,d\tau \qquad \text{(E.4)}$$

Therefore, solving equation (E.2) for C_{im} in terms of C_m gives

$$C_{im}(X,T)=e^{-\alpha T}C_{im,0}(X)+\alpha e^{-\alpha T}\int_0^T e^{\alpha\tau}C_m(X,\tau)\,d\tau \qquad \text{(E.5)}$$

Taking d/dT of both sides gives

$$\frac{\partial C_{im}(X,T)}{\partial T}=-\alpha e^{-\alpha T}C_{im,0}(X)-\alpha^2e^{-\alpha T}\int_0^T e^{\alpha\tau}C_m(X,\tau)\,d\tau+\alpha C_m(X,T) \qquad \text{(E.6)}$$

Plugging equation (E.6) into (E.1) results in the contaminant transport equation

$$\begin{aligned}\frac{\partial C_m(X,T)}{\partial T}=&\left(\frac{Q(T)}{X}+D\right)\frac{\partial^2 C_m(X,T)}{\partial X^2}+\left(\frac{Q(T)}{X}+\frac{D}{X}\right)\frac{\partial C_m(X,T)}{\partial X}-\beta\alpha C_m(X,T)\\&+\beta\alpha e^{-\alpha T}C_{im,0}(X)+\beta\alpha^2e^{-\alpha T}\int_0^T e^{\alpha\tau}C_m(X,\tau)\,d\tau\end{aligned} \qquad \text{(E.7)}$$

or

$$0=\left(\frac{Q(T)}{X}+D\right)\frac{\partial^2 C_m(X,T)}{\partial X^2}+\left(\frac{Q(T)}{X}+\frac{D}{X}\right)\frac{\partial C_m(X,T)}{\partial X}-\beta\alpha C_m(X,T)$$
$$+\beta\alpha e^{-\alpha T}C_{im,0}(X)+\beta\alpha^2 e^{-\alpha T}\int_0^T e^{\alpha\tau}C_m(X,\tau)\,d\tau-\frac{\partial C_m(X,T)}{\partial T} \tag{E.8}$$

Forming the Lagrangian in differential form results in

$$\ell=\int_0^{T_{final}} f(T,Q(T),C_m(X_w,T))\,dT+$$
$$\int_0^{T_{final}}\int_{X_w}^{\infty}\lambda(X,T)\begin{bmatrix}G[C_m](X,T)+\beta\alpha e^{-\alpha T}C_{im,0}(X)\\ +\beta\alpha^2 e^{-\alpha T}\int_0^T e^{\alpha\tau}C_m(X,\tau)\,d\tau-\dfrac{\partial C_m}{\partial T}\end{bmatrix}dXdT \tag{E.9}$$

where $G[C_m](X,T)$ is defined to be the differential operator which depends on Q,

$$G[C_m](X,T)\equiv\left(\frac{Q(T)}{X}+D\right)\frac{\partial^2 C_m}{\partial X^2}+\left(\frac{Q(T)}{X}+\frac{D}{X}\right)\frac{\partial C_m}{\partial X}-\beta\alpha C_m \tag{E.10}$$

Note that equation (E.9) has seven terms which can be simplified by performing integration by parts on each term. Starting with the second term

$$\int_0^{T_{final}}\int_{X_w}^{\infty}\lambda(X,T)\left(\frac{Q(T)}{X}+D\right)\frac{\partial^2 C_m}{\partial X^2}\,dXdT \tag{E.11}$$

performing integration by parts with respect to X results in

$$=\lambda(X,T)\left(\frac{Q(T)}{X}+D\right)\frac{\partial C_m}{\partial X}\Bigg[_{X_w}^{\infty}-\int_{X_w}^{\infty}\frac{\partial C_m}{\partial X}\frac{\partial}{\partial X}\left[\lambda(X,T)\left(\frac{Q(T)}{X}+D\right)\right]dX \tag{E.12}$$

Evaluating at X_w and ∞ gives,

$$=\lambda(\infty,T)D\frac{\partial C_m}{\partial X}(\infty,T)-\lambda(X_w,T)\left(\frac{Q(T)}{X_w}+D\right)\frac{\partial C_m}{\partial X}(X_w,T)$$
$$-\int_{X_w}^{\infty}\frac{\partial C_m}{\partial X}\frac{\partial}{\partial X}\left[\lambda(X,T)\left(\frac{Q(T)}{X}+D\right)\right]dX \tag{E.13}$$

Performing integration by parts once again to simplify further results in

$$= \lambda(\infty,T)\,D\frac{\partial C_m}{\partial X}(\infty,T) - \frac{\partial}{\partial X}\left[\lambda(X,T)\left(\frac{Q(T)}{X}+D\right)\right]C_m(X,T)\Bigg[_{X_w}^{\infty} + \int_{X_w}^{\infty} C_m \frac{\partial^2}{\partial X^2}\left[\lambda(X,T)\left(\frac{Q(T)}{X}+D\right)\right]dX \tag{E.14}$$

$$= \lambda(\infty,T)\,D\frac{\partial C_m}{\partial X}(\infty,T) - \left[\frac{\partial}{\partial X}\left(\frac{Q(T)}{X}+D\right) - \frac{Q(T)}{X^2}\lambda(X,T)\right]C_m(X,T)\Bigg[_{X_w}^{\infty} + \int_{X_w}^{\infty} C_m \frac{\partial^2}{\partial X^2}\left[\lambda(X,T)\left(\frac{Q(T)}{X}+D\right)\right]dX \tag{E.15}$$

Evaluating at X_w and ∞ gives,

$$\lambda(\infty,T)\,D\frac{\partial C_m}{\partial X}(\infty,T) - \left[\frac{\partial \lambda}{\partial X}(\infty,T)D\right]C_m(\infty,T) + \left[\frac{\partial \lambda}{\partial X}\left(\frac{Q(T)}{X_w}+D\right) - \lambda(X,T)\frac{Q(T)}{X^2}\right]C_m(X,T) + \int_{X_w}^{\infty} C_m(X,T)\frac{\partial^2}{\partial X^2}\left[\lambda(X,T)\left(\frac{Q(T)}{X}+D\right)\right]dX \tag{E.16}$$

Knowing that the boundary condition at ∞ for C_m is

$$\frac{\partial C_m}{\partial X}(\infty,T) + C_m(\infty,T) = 0 \tag{E.17}$$

then equation (E.16) simplifies to

$$-\lambda(\infty,T)\,DC_m(\infty,T) - \frac{\partial \lambda}{\partial X}(\infty,T)\,DC_m(\infty,T) \tag{E.18}$$

Collecting all the terms results in the final form of equation (E.11)

$$-DC_m(\infty,T)\left[\lambda(\infty,T) + \frac{\partial \lambda}{\partial X}(\infty,T)\right] + \left[\frac{\partial \lambda}{\partial X}(X_w,T)\left(\frac{Q(T)}{X_w}+D\right) - \lambda(X,T)\frac{Q(T)}{X^2}\right]C_m(X,T) + \int_{X_w}^{\infty} C_m(X,T)\frac{\partial^2}{\partial X^2}\left[\lambda(X,T)\left(\frac{Q(T)}{X}+D\right)\right]dX \tag{E.19}$$

Evaluating the third term of equation (E.9)

$$\int_0^{T_{final}} \int_{X_w}^{\infty} \lambda(X,T)\left(\frac{Q(T)}{X}+\frac{D}{X}\right)\frac{\partial C_m}{\partial X}\,dXdT \qquad \text{(E.20)}$$

and performing integration by parts results in

$$\lambda(X,T)\left(\frac{Q(T)}{X}+D\right)C_m\Big|_{X_w}^{\infty} - \int_{X_w}^{\infty} C_m \frac{\partial}{\partial X}\left[\lambda(X,T)\left(\frac{Q(T)}{X}+\frac{D}{X}\right)\right]dX \qquad \text{(E.21)}$$

Evaluating at X_w and ∞ gives results in the final form of the third term in equation (E.8)

$$-\lambda(X_w,T)\left(\frac{Q(T)}{X_w}+\frac{D}{X_w}\right)C_m(X_w,T) - \int_{X_w}^{\infty} C_m \frac{\partial}{\partial X}\left[\lambda(X,T)\left(\frac{Q(T)}{X}+\frac{D}{X}\right)\right]dX \qquad \text{(E.22)}$$

The fourth and fifth terms do not require integration by parts and are written as

$$\int_0^{T_{final}} \int_{X_w}^{\infty} \lambda(X,T)\left[-\beta\alpha\, C_m(X,T)\right]dXdT \qquad \text{(E.23)}$$

and

$$\int_0^{T_{final}} \int_{X_w}^{\infty} \lambda(X,T)\beta\alpha e^{-\alpha T}\, C_{im,0}(X)\,dXdT \qquad \text{(E.24)}$$

Looking at the sixth term

$$\int_0^{T_{final}} \int_{X_w}^{\infty} \lambda(X,T)\alpha^2\beta e^{-\alpha T}\int_0^T e^{\alpha\tau}\, C_m(X,\tau)\,d\tau\, dXdT \qquad \text{(E.25)}$$

and interchanging the X and T integration is

$$\int_{X_w}^{\infty} \alpha^2\beta \int_0^{T_{final}} \lambda(X,T)e^{-\alpha T}\int_0^T e^{\alpha\tau}\, C_m(X,\tau)\,d\tau\, dTdX \qquad \text{(E.26)}$$

Ignoring the constants for the moment and the integration with respect to X, and performing integration by parts with respect to T where $du = e^{\alpha T}\, C_m(X,T)$ and $v = \int_0^T \lambda(X,t)e^{-\alpha t}\,dt$, then $\int udv = uv - \int vdu$ is equal to

$$\left(\int_0^T e^{\alpha\tau}\, C_m(X,\tau)\, d\tau\right)\left(\int_0^T \lambda(X,t) e^{-\alpha t}\, dt\right)\Big|_{T=0}^{T=T_{final}} - \int_0^{T_{final}} \left(\int_0^T \lambda(X,t) e^{-\alpha t}\, dt\right) e^{\alpha T}\, C_m(X,T)\, dT$$

(E.27)

Evaluating at $T = T_{final}$ and $T = 0$ results in

$$\left(\int_0^{T_{final}} e^{\alpha\tau}\, C_m(X,\tau)\, d\tau\right)\left(\int_0^{T_{final}} \lambda(X,t) e^{-\alpha t}\, dt\right) - 0 - \int_0^{T_{final}} e^{\alpha T}\, C_m(X,T) \int_0^T \lambda(X,t) e^{-\alpha t}\, dt\, dT$$

(E.28)

$$= \int_0^{T_{final}} \int_0^{T_{final}} e^{\alpha\tau} e^{-\alpha t}\, C_m(X,\tau) \lambda(X,t)\, dt\, d\tau - \int_0^{T_{final}} \int_0^T e^{\alpha T} e^{-\alpha t}\, C_m(X,T) \lambda(X,t)\, dT dt$$

(E.29)

In the first integral of equation (E.29), change the integration variable τ to T to get

$$\int_0^{T_{final}} \int_0^{T_{final}} e^{\alpha T} e^{-\alpha t}\, C_m(X,T) \lambda(X,t)\, dt dT - \int_0^{T_{final}} \int_0^T e^{\alpha T} e^{-\alpha t}\, C_m(X,T) \lambda(X,t) dt dT$$

(E.30)

$$= \int_0^{T_{final}} \left[\int_0^{T_{final}} e^{\alpha T} e^{-\alpha t}\, C_m(X,T) \lambda(X,t)\, dt - \int_0^T e^{\alpha T} e^{-\alpha t}\, C_m(X,T) \lambda(X,t) dt\right] dT$$

(E.31)

Since the integrands are the same in both integrals then this simplifies to

$$\int_0^{T_{final}} \int_T^{T_{final}} e^{\alpha T} e^{-\alpha t}\, C_m(X,T) \lambda(X,t)\, dt dT \qquad \text{(E.32)}$$

Rearranging equation (E.32) and plugging in the constants from the original equation (E.25) results in the sixth term's final form

$$\int_0^{T_{final}} \int_{X_w}^{\infty} \alpha^2 \beta C_m(X,T) e^{\alpha T} \left(\int_T^{T_{final}} e^{-\alpha t} \lambda(X,t)\, dt\right) dX dT \qquad \text{(E.33)}$$

Lastly, the seventh term

$$\int_0^{T_{final}} \int_{X_w}^{\infty} \lambda(X,T) \left[-\frac{\partial C_m}{\partial T}\right] dX dT \qquad \text{(E.34)}$$

is simplified by first interchanging the X and T integration

$$\int_{X_w}^{\infty}\int_{0}^{T_{final}} \lambda(X,T)\left[-\frac{\partial C_m}{\partial T}\right] dT dX \qquad \text{(E.35)}$$

and then by performing is integration by parts

$$\lambda(X,T)\left(-C_m(X,T)\right)\Big|_0^{T_{final}} + \int_0^{T_{final}} C_m(X,T)\frac{\partial \lambda}{\partial T}(X,T)\, dT \qquad \text{(E.36)}$$

Evaluating at $T = T_{final}$ and $T = 0$ results in the seventh term's final form as

$$-\lambda(X,T_{final})C_m(X,T_{final}) + \lambda(X,0)C_{m,0}(X) + \int_0^{T_{final}} C_m(X,T)\frac{\partial \lambda}{\partial T}(X,T)\, dT \qquad \text{(E.37)}$$

Collecting all the new terms (i.e., equations (E.19), (E.22), (E.23), (E.24), (E.33), and (E.37)) and forming the Lagrangian in differential form results in

$$\begin{aligned}
\mathcal{L} &= \int_0^{T_{final}} f(T,Q(T),C_m(X_w,T))dT \\
&+\int_0^{T_{final}}\left\{-DC_m(\infty,T)\left[\lambda(\infty,T)+\frac{\partial\lambda}{\partial X}(\infty,T)\right]+\left[\frac{\partial\lambda}{\partial X}(X_w,T)\left(\frac{Q(T)}{X_w}+D\right)-\lambda(X_w,T)\frac{Q(T)}{X_w^{\,2}}\right]\right\}C_m(X_w,T)dT \\
&+\int_0^{T_{final}}\int_{X_w}^{\infty}\frac{\partial^2}{\partial X^2}\left[\lambda(X,T)\left(\frac{Q(T)}{X}+D\right)\right]C_m(X,T)dX\,dT \\
&-\int_0^{T_{final}}\lambda(X_w,T)\left(\frac{Q(T)}{X_w}+\frac{D}{X_w}\right)C_m(X_w,T)dT-\int_0^{T_{final}}\int_{X_w}^{\infty}\frac{\partial}{\partial X}\left[\lambda(X,T)\left(\frac{Q(T)}{X}+\frac{D}{X}\right)\right]C_m(X,T)dXdT \\
&+\int_0^{T_{final}}\int_{X_w}^{\infty}\lambda(X,T)\left[-\beta\alpha\, C_m(X,T)\right]dXdT \\
&+\int_0^{T_{final}}\int_{X_w}^{\infty}\lambda(X,T)\beta\alpha e^{-\alpha T}\, C_{im,0}(X)\,dXdT \\
&+\int_0^{T_{final}}\int_{X_w}^{\infty}\alpha^2\beta C_m(X,T)e^{\alpha T}\left(\int_T^{T_{final}}e^{-\alpha t}\lambda(X,t)\,dt\right)dT \\
&-\int_{X_w}^{\infty}\lambda(X,T_{final})C_m(X,T_{final})dX+\int_{X_w}^{\infty}\lambda(X,0)C_{m,0}(X)dX+\int_{X_w}^{\infty}\int_0^{T_{final}}C_m(X,T)\frac{\partial\lambda}{\partial T}(X,T)\,dT\,dX
\end{aligned}$$

(E.38)

Simplifying equation (E.38) by collecting similar terms yields

$$
\begin{aligned}
\mathcal{L} = & \int_0^{T_{final}} f(T, Q(T), C_m(X_w, T))\,dT \\
& + \int_0^{T_{final}} \int_{X_w}^{\infty} C_m(X,T) \left\{ \begin{aligned} & \frac{\partial \lambda}{\partial T}(X,T) + \frac{\partial^2}{\partial X^2}\left[\lambda(X,T)\left(\frac{Q(T)}{X} + D\right)\right] - \frac{\partial}{\partial X}\left[\lambda(X,T)\left(\frac{Q(T)}{X} + \frac{D}{X}\right)\right] \\ & - \beta\alpha\lambda(X,T) + \alpha^2 \beta e^{\alpha T}\left(\int_T^{T_{final}} e^{-\alpha t}\lambda(X,t)\,dt\right) \end{aligned} \right\} dX dT \\
& + \int_0^{T_{final}} \int_{X_w}^{\infty} \beta\alpha e^{-\alpha T} \lambda(X,T) C_{im,0}(X)\,dX dT \\
& - \int_0^{T_{final}} D C_m(\infty,T)\left[\lambda(\infty,T) + \frac{\partial \lambda}{\partial X}(\infty,T)\right] dT \\
& + \int_0^{T_{final}} C_m(X_w,T)\left\{\frac{\partial \lambda}{\partial X}(X_w,T)\left(\frac{Q(T)}{X_w} + D\right) - \lambda(X_w,T)\left(\frac{Q(T)}{X_w} + \frac{D}{X_w}\right) - \lambda(X_w,T)\frac{Q(T)}{X_w^{\,2}}\right\} dT \\
& - \int_{X_w}^{\infty} \lambda(X, T_{final}) C_m(X, T_{final})\,dX + \int_{X_w}^{\infty} \lambda(X,0) C_{m,0}(X)\,dX
\end{aligned}
\tag{E.39}
$$

With the Lagrangian in two forms both the abbreviated version (equation E.9) and the expanded version (equation E.39) and noting that the Lagrangian is subject to various constraints, we next take the variation of the Lagrangian with respect to each variable i.e., C_m, λ ,and Q. We start with the variation of $\mathcal{L}$ with respect to C_m which is defined to be

$$
\delta\mathcal{L}[Q, C_m, \lambda; 0, h, 0] = \lim_{a \to 0} \frac{d}{da} \mathcal{L}[Q, C_m + ah, \lambda] \tag{E.40}
$$

Applying this process to the Lagrangian in equation (E.39) results in the following

$$\delta\mathcal{L}[Q,C_m,\lambda;0,h,0]=\int_0^{T_{final}}\frac{\partial f}{\partial C}[T,Q(t),C_m(X_w,T)]h(X_w,T)dT$$

$$+\int_0^{T_{final}}\int_{X_w}^{\infty}h(X,T)\left\{\begin{array}{l}\frac{\partial\lambda}{\partial T}(X,T)+\frac{\partial^2}{\partial X^2}\left[\lambda(X,T)\left(\frac{Q(t)}{X}+D\right)\right]-\frac{\partial}{\partial X}\left[\lambda(X,T)\left(\frac{Q(t)}{X}+\frac{D}{X}\right)\right]\\ -\beta\alpha\lambda(X,T)+\alpha^2\beta e^{\alpha T}\left(\int_T^{T_{final}}e^{-\alpha t}\lambda(X,t)dt\right)\end{array}\right\}dXdT$$

$$-\int_0^{T_{final}}Dh(\infty,T)\left[\lambda(\infty,T)+\frac{\partial\lambda}{\partial X}(\infty,T)\right]dT$$

$$+\int_0^{T_{final}}h(X_w,T)\left\{\frac{\partial\lambda}{\partial X}(X_w,T)\left(\frac{Q(t)}{X_w}+D\right)-\lambda(X_w,T)\left(\frac{Q(t)}{X_w}+\frac{D}{X_w}\right)-\lambda(X_w,T)\frac{Q(t)}{X_w^{\,2}}\right\}dT$$

$$-\int_{X_w}^{\infty}\lambda(X,T_{final})h(X,T_{final})dX$$

(E.41)

Next we take the variation of $\mathcal{L}$ with respect to λ using equation (E.9) and

$$\delta\mathcal{L}[Q,C_m,\lambda;0,0,\mu]=\lim_{a\to 0}\frac{d}{da}\mathcal{L}[Q,C_m,\lambda+a\mu] \qquad \text{(E.42)}$$

then

$$\delta\mathcal{L}[Q,C_m,\lambda;0,0,\mu]=\int_0^{T_{final}}\int_{X_w}^{\infty}\mu(X,T)\left[\begin{array}{l}G[C_m]+\beta\alpha e^{-\alpha T}C_{im,0}(X)\\ +\beta\alpha^2e^{-\alpha T}\int_0^T e^{\alpha\tau}C_m(X,\tau)d\tau-\frac{\partial C_m}{\partial T}\end{array}\right]dXdT$$

(E.43)

Lastly, we take the variation of $\mathcal{L}$ with respect to Q. This is equivalent to the derivative of $\mathcal{L}$ with respect to the switching times T_1 and T_2. But first we rewrite equation (E.39) where Q(T) represents pulsed pumping where Q(T) = 1 when evaluated between $0 < T < T_1$, Q(T) = 0 when evaluated between $T_1 < T < T_2$, and Q(T) = 1 when evaluated between $T_2 < T < T_3$ where $T_3 = T_{final}$.

Define $C_m^{(i)}$ for i = 1, 2, 3 by

$$
C_m(X,T)=\begin{cases} C_m^{(1)}(X,T) & \text{for} \quad 0\le T\le T_1 \\ C_m^{(2)}(X,T) & \text{for} \quad T_1<T\le T_2 \\ C_m^{(3)}(X,T) & \text{for} \quad T_2<T\le T_3 \end{cases} \tag{E.44}
$$

Similarly, define $\lambda^{(i)}$ for $i = 1, 2, 3$ by

$$
\lambda(X,T)=\begin{cases} \lambda^{(1)}(X,T) & \text{for} \quad 0\le T\le T_1 \\ \lambda^{(2)}(X,T) & \text{for} \quad T_1<T\le T_2 \\ \lambda^{(3)}(X,T) & \text{for} \quad T_2<T\le T_3 \end{cases} \tag{E.45}
$$

Evaluating (E.39) using (E.44) and (E.45) results in results in

$$
\begin{aligned}
\mathcal{L} = {} & \int_0^{T_1} f\left[T,1,C_m^{(1)}(X_w,T)\right]dT-\int_{T_1}^{T_2} f\left[T,0,C_m^{(2)}(X_w,T)\right]dT+\int_{T_2}^{T_3} f\left[T,1,C_m^{(3)}(X_w,T)\right]dT \\
& +\int_0^{T_1}\int_{X_w}^{\infty} C_m^{(1)}(X,T)\left\{\begin{aligned} & \frac{\partial\lambda^{(1)}}{\partial T}(X,T)+\frac{\partial^2}{\partial X^2}\left[\lambda^{(1)}(X,T)\left(\frac{1}{X}+D\right)\right]-\frac{\partial}{\partial X}\left[\lambda^{(1)}(X,T)\left(\frac{1}{X}+\frac{D}{X}\right)\right] \\ & -\beta\alpha\lambda^{(1)}(X,T)+\alpha^2\beta e^{\alpha T}\left[\begin{aligned} & \int_T^{T_1} e^{-\alpha t}\lambda^{(1)}(X,t)\,dt+\int_{T_1}^{T_2} e^{-\alpha t}\lambda^{(2)}(X,t)\,dt \\ & +\int_{T_2}^{T_3} e^{-\alpha t}\lambda^{(3)}(X,t)\,dt \end{aligned}\right] \end{aligned}\right\}dXdT \\
& +\int_{T_1}^{T_2}\int_{X_w}^{\infty} C_m^{(2)}(X,T)\left\{\begin{aligned} & \frac{\partial\lambda^{(2)}}{\partial T}(X,T)+\frac{\partial^2}{\partial X^2}\left[\lambda^{(2)}(X,T)D\right]-\frac{\partial}{\partial X}\left[\lambda^{(2)}(X,T)\frac{D}{X}\right] \\ & -\beta\alpha\lambda^{(2)}(X,T)+\alpha^2\beta e^{\alpha T}\left[\int_T^{T_2} e^{-\alpha t}\lambda^{(2)}(X,t)\,dt+\int_{T_2}^{T_3} e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\right] \end{aligned}\right\}dXdT \\
& +\int_{T_2}^{T_3}\int_{X_w}^{\infty} C_m^{(3)}(X,T)\left\{\begin{aligned} & \frac{\partial\lambda^{(3)}}{\partial T}(X,T)+\frac{\partial^2}{\partial X^2}\left[\lambda^{(3)}(X,T)\left(\frac{1}{X}+D\right)\right]-\frac{\partial}{\partial X}\left[\lambda^{(3)}(X,T)\left(\frac{1}{X}+\frac{D}{X}\right)\right] \\ & -\beta\alpha\lambda^{(3)}(X,T)+\alpha^2\beta e^{\alpha T}\int_T^{T_3} e^{-\alpha t}\lambda^{(3)}(X,t)\,dt \end{aligned}\right\}dXdT \\
& -\int_0^{T_1} DC_m^{(1)}(\infty,T)\left[\lambda^{(1)}(\infty,T)+\frac{\partial\lambda^{(1)}}{\partial X}(\infty,T)\right]dT-\int_{T_1}^{T_2} DC_m^{(2)}(\infty,T)\left[\lambda^{(2)}(\infty,T)+\frac{\partial\lambda^{(2)}}{\partial X}(\infty,T)\right]dT \\
& -\int_{T_2}^{T_3} DC_m^{(3)}(\infty,T)\left[\lambda^{(3)}(\infty,T)+\frac{\partial\lambda^{(3)}}{\partial X}(\infty,T)\right]dT
\end{aligned}
$$

$$+\int_0^{T_1} C_m^{(1)}(X_w,T)\left\{\frac{\partial\lambda^{(1)}}{\partial X}(X_w,T)\left(\frac{1}{X_w}+D\right)-\lambda^{(1)}(X_w,T)\left(\frac{1}{X_w}+\frac{D}{X_w}\right)-\lambda^{(1)}(X_w,T)\frac{1}{X_w^{\,2}}\right\}dT$$
$$+\int_{T_1}^{T_2} C_m^{(2)}(X_w,T)\left\{\frac{\partial\lambda^{(2)}}{\partial X}(X_w,T)D-\lambda^{(2)}(X_w\ T)\frac{D}{X_w}\right\}dT$$
$$+\int_{T_2}^{T_3} C_m^{(3)}(X_w,T)\left\{\frac{\partial\lambda^{(3)}}{\partial X}(X_w,T)\left(\frac{1}{X_w}+D\right)-\lambda^{(3)}(X_w,T)\left(\frac{1}{X_w}+\frac{D}{X_w}\right)-\lambda^{(3)}(X_w,T)\frac{1}{X_w^{\,2}}\right\}dT$$
$$-\int_{X_w}^{\infty}\lambda^{(3)}(X,T_{final})C_m^{(3)}(X,T)\,dX$$

(E.46)

Taking the derivative of $\mathcal{L}$ with respect to T_1 results in

$$\frac{\partial}{\partial T_1}\mathcal{L}=f\left[T_1,1,C_m^{(1)}(X_w,T_1)\right]-f\left[T_1,0,C_m^{(2)}(X_w,T_1)\right]$$
$$+\int_{X_w}^{\infty} C_m^{(1)}(X,T_1)\left\{\begin{array}{l}\frac{\partial\lambda^{(1)}}{\partial T}(X,T_1)+\frac{\partial^2}{\partial X^2}\left[\lambda^{(1)}(X,T_1)\left(\frac{1}{X}+D\right)\right]-\frac{\partial}{\partial X}\left[\lambda^{(1)}(X,T_1)\left(\frac{1}{X}+\frac{D}{X}\right)\right]\\ -\beta\alpha\lambda^{(1)}(X,T_1)+\alpha^2\beta e^{\alpha T_1}\left[\int_{T_1}^{T_2}e^{-\alpha t}\lambda^{(2)}(X,t)\,dt+\int_{T_2}^{T_3}e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\right]\end{array}\right\}dX$$
$$-\int_{X_w}^{\infty} C_m^{(2)}(X,T_1)\left\{\begin{array}{l}\frac{\partial\lambda^{(2)}}{\partial T}(X,T_1)+\frac{\partial^2}{\partial X^2}\left[\lambda^{(2)}(X,T_1)D\right]-\frac{\partial}{\partial X}\left[\lambda^{(2)}(X,T_1)\frac{D}{X}\right]\\ -\beta\alpha\lambda^{(2)}(X,T_1)+\alpha^2\beta e^{\alpha T_1}\left[\int_{T_1}^{T_2}e^{-\alpha t}\lambda^{(2)}(X,t)\,dt+\int_{T_2}^{T_3}e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\right]\end{array}\right\}dX$$

$$-DC_m^{(1)}(\infty,T_1)\left[\lambda^{(1)}(\infty,T_1)+\frac{\partial\lambda^{(1)}}{\partial X}(\infty,T_1)\right]+DC_m^{(2)}(\infty,T_1)\left[\lambda^{(2)}(\infty,T_1)+\frac{\partial\lambda^{(2)}}{\partial X}(\infty,T_1)\right]$$
$$+C_m^{(1)}(X_w,T_1)\left\{\frac{\partial\lambda^{(1)}}{\partial X}(X_w,T_1)\left(\frac{1}{X_w}+D\right)-\lambda^{(1)}(X_w,T_1)\left(\frac{1}{X_w}+\frac{D}{X_w}\right)-\lambda^{(1)}(X_w,T_1)\frac{1}{X_w^{\,2}}\right\}$$
$$-C_m^{(2)}(X_w,T_1)\left\{\frac{\partial\lambda^{(2)}}{\partial X}(X_w,T_1)D-\lambda^{(2)}(X_w,T_1)\frac{D}{X_w}\right\}$$

(E.47)

Taking the derivative of $\mathcal{L}$ with respect to T_2 results in

$$
\begin{aligned}
\frac{\partial}{\partial T_2}\ell &= f\left[T_2,0,C_m^{(2)}(X_w,T_2)\right]-f\left[T_2,1,C_m^{(3)}(X_w,T_2)\right]\\
&+\int_{X_w}^{\infty} C_m^{(2)}(X,T_2)\left\{\begin{aligned}&\frac{\partial\lambda^{(2)}}{\partial T}(X,T_2)+\frac{\partial^2}{\partial X^2}\left[\lambda^{(2)}(X,T_2)D\right]-\frac{\partial}{\partial X}\left[\lambda^{(2)}(X,T_2)\frac{D}{X}\right]\\&-\beta\alpha\lambda^{(2)}(X,T_2)+\alpha^2\beta e^{\alpha T_2}\int_{T_2}^{T_3}e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\end{aligned}\right\}dX\\
&-\int_{X_w}^{\infty} C_m^{(3)}(X,T_2)\left\{\begin{aligned}&\frac{\partial\lambda^{(3)}}{\partial T}(X,T_2)+\frac{\partial^2}{\partial X^2}\left[\lambda^{(3)}(X,T_2)\left(\frac{1}{X}+D\right)\right]-\frac{\partial}{\partial X}\left[\lambda^{(3)}(X,T_2)\left(\frac{1}{X}+\frac{D}{X}\right)\right]\\&-\beta\alpha\lambda^{(3)}(X,T_2)+\alpha^2\beta e^{\alpha T_2}\int_{T_2}^{T_3}e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\end{aligned}\right\}dX\\
&-DC_m^{(2)}(\infty,T_2)\left[\lambda^{(2)}(\infty,T_2)+\frac{\partial\lambda^{(2)}}{\partial X}(\infty,T_2)\right]+DC_m^{(3)}(\infty,T_2)\left[\lambda^{(3)}(\infty,T_2)+\frac{\partial\lambda^{(3)}}{\partial X}(\infty,T_2)\right]\\
&+C_m^{(2)}(X_w,T_2)\left\{\frac{\partial\lambda^{(2)}}{\partial X}(X_w,T_2)D-\lambda^{(2)}(X_w,T_2)\frac{D}{X_w}\right\}\\
&-C_m^{(3)}(X_w,T_2)\left\{\frac{\partial\lambda^{(3)}}{\partial X}(X_w,T_2)\left(\frac{1}{X_w}+D\right)-\lambda^{(3)}(X_w,T_2)\left(\frac{1}{X_w}+\frac{D}{X_w}\right)-\lambda^{(3)}(X_w,T_2)\frac{1}{{X_w}^2}\right\}
\end{aligned}
\tag{E.48}
$$

Appendix F

With the first variations determined for each independent variable, the second variation must be determined in order to determine the necessary and sufficient optimality conditions for our problem.

Referencing the first variation of $\mathcal{L}$ with respect to λ in the direction of μ equation (E.45), it is easy to determine the second variation of $\mathcal{L}$ with respect to λ in the direction of μ which is by definition

$$\delta^2\mathcal{L}[Q, C_m, \lambda; 0, 0, \mu] = \lim_{a\to 0}\frac{1}{2}\frac{d^2}{da^2}\mathcal{L}[Q, C_m, \lambda + a\,\mu] = 0 \tag{F.1}$$

Additionally, utilizing the first variation of $\mathcal{L}$ with respect to C_m in the direction of h, equation (E.41), it is easy to determine the second variation of $\mathcal{L}$ with respect to C_m in the direction of h as,

$$\delta^2\mathcal{L}[Q, C_m, \lambda; 0, h, 0] = \lim_{a\to 0}\frac{1}{2}\frac{d^2}{da^2}\mathcal{L}[Q, C + ah, \lambda] = \int_0^{T_{final}}\frac{\partial^2 f}{\partial C^2}[T, Q(t), C_m(X_w, T)]\,h^2(X_w, T)\,dT \tag{F.2}$$

Unlike the previous derivations the second variation of $\mathcal{L}$ with respect to Q is more complicated and can be evaluated by examining the second derivative of $\mathcal{L}$ with respect to T_1 and T_2. First, the second derivative of $\mathcal{L}$ with respect to T_1 is accomplished by referencing equation (E.49).

$$
\begin{aligned}
\frac{\partial^2}{\partial T_1^{\,2}}\mathcal{L} &= \frac{\partial f}{\partial T}\left[T_1,1,C_m^{(1)}(X_w,T_1)\right]+\frac{\partial f}{\partial C}\left[T_1,1,C_m^{(1)}(X_w,T_1)\right]\frac{\partial C_m^{(1)}}{\partial T}(X_w,T_1)\\
&-\frac{\partial f}{\partial T}\left[T_1,0,C_m^{(2)}(X_w,T_1)\right]-\frac{\partial f}{\partial C}\left[T_1,0,C_m^{(2)}(X_w,T_1)\right]\frac{\partial C_m^{(2)}}{\partial T}(X_w,T_1)\\
&+\int_{X_w}^{\infty}\frac{\partial C_m^{(1)}}{\partial T}(X,T_1)\left\{\begin{array}{l}
\dfrac{\partial \lambda^{(1)}}{\partial T}(X,T_1)+\dfrac{\partial^2}{\partial X^2}\left[\lambda^{(1)}(X,T_1)\left(\dfrac{1}{X}+D\right)\right]-\dfrac{\partial}{\partial X}\left[\lambda^{(1)}(X,T_1)\left(\dfrac{1}{X}+\dfrac{D}{X}\right)\right]\\
-\beta\alpha\lambda^{(1)}(X,T_1)+\alpha^2\beta e^{\alpha T_1}\left[\int_{T_1}^{T_2}e^{-\alpha t}\lambda^{(2)}(X,t)\,dt+\int_{T_2}^{T_3}e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\right]
\end{array}\right\}dX\\
&+\int_{X_w}^{\infty}C_m^{(1)}(X,T_1)\left\{\begin{array}{l}
\dfrac{\partial^2 \lambda^{(1)}}{\partial T^2}(X,T_1)+\dfrac{\partial^2}{\partial X^2}\left[\dfrac{\partial \lambda^{(1)}}{\partial T}(X,T_1)\left(\dfrac{1}{X}+D\right)\right]-\dfrac{\partial}{\partial X}\left[\dfrac{\partial \lambda^{(1)}}{\partial T}(X,T_1)\left(\dfrac{1}{X}+\dfrac{D}{X}\right)\right]\\
-\beta\alpha\dfrac{\partial \lambda^{(1)}}{\partial T}(X,T_1)+\alpha^3\beta e^{\alpha T_1}\left[\int_{T_1}^{T_2}e^{-\alpha t}\lambda^{(2)}(X,t)\,dt+\int_{T_2}^{T_3}e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\right]\\
-\alpha^2\beta e^{\alpha T_1}\left[e^{-\alpha T_1}\lambda^{(2)}(X,T_1)\right]
\end{array}\right\}dX\\
&-\int_{X_w}^{\infty}\frac{\partial C_m^{(2)}}{\partial T}(X,T_1)\left\{\begin{array}{l}
\dfrac{\partial \lambda^{(2)}}{\partial T}(X,T_1)+\dfrac{\partial^2}{\partial X^2}\left[\lambda^{(2)}(X,T_1)D\right]-\dfrac{\partial}{\partial X}\left[\lambda^{(2)}(X,T_1)\dfrac{D}{X}\right]\\
-\beta\alpha\lambda^{(2)}(X,T_1)+\alpha^2\beta e^{\alpha T_1}\left[\int_{T_1}^{T_2}e^{-\alpha t}\lambda^{(2)}(X,t)\,dt+\int_{T_2}^{T_3}e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\right]
\end{array}\right\}dX\\
&-\int_{X_w}^{\infty}C_m^{(2)}(X,T_1)\left\{\begin{array}{l}
\dfrac{\partial^2 \lambda^{(2)}}{\partial T^2}(X,T_1)+\dfrac{\partial^2}{\partial X^2}\dfrac{\partial \lambda^{(2)}}{\partial T}(X,T_1)D-\dfrac{\partial}{\partial X}\left[\dfrac{\partial \lambda^{(2)}}{\partial T}(X,T_1)\dfrac{D}{X}\right]\\
-\beta\alpha\dfrac{\partial \lambda^{(2)}}{\partial T}(X,T_1)+\alpha^3\beta e^{\alpha T_1}\left[\int_{T_1}^{T_2}e^{-\alpha t}\lambda^{(2)}(X,t)\,dt+\int_{T_2}^{T_3}e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\right]\\
-\alpha^2\beta e^{\alpha T_1}\left[e^{-\alpha T_1}\lambda^{(2)}(X,T_1)\right]
\end{array}\right\}dX\\
&-D\frac{\partial C_m^{(1)}}{\partial T}(\infty,T_1)\left[\lambda^{(1)}(\infty,T_1)+\frac{\partial \lambda^{(1)}}{\partial X}(\infty,T_1)\right]-DC_m^{(1)}(\infty,T_1)\left[\frac{\partial \lambda^{(1)}}{\partial T}(\infty,T_1)+\frac{\partial}{\partial X}\frac{\partial \lambda^{(1)}}{\partial T}(\infty,T_1)\right]\\
&+D\frac{\partial C_m^{(2)}}{\partial T}(\infty,T_1)\left[\lambda^{(2)}(\infty,T_1)+\frac{\partial \lambda^{(2)}}{\partial X}(\infty,T_1)\right]+DC_m^{(2)}(\infty,T_1)\left[\frac{\partial \lambda^{(2)}}{\partial T}(\infty,T_1)+\frac{\partial}{\partial X}\frac{\partial \lambda^{(2)}}{\partial T}(\infty,T_1)\right]\\
&+\frac{\partial C_m^{(1)}}{\partial T}(X_w,T_1)\left\{\frac{\partial \lambda^{(1)}}{\partial X}(X_w,T_1)\left(\frac{1}{X_w}+D\right)-\lambda^{(1)}(X_w,T_1)\left(\frac{1}{X_w}+\frac{D}{X_w}\right)-\lambda^{(1)}(X_w,T_1)\frac{1}{X_w^{\,2}}\right\}\\
&+C_m^{(1)}(X_w,T_1)\left\{\frac{\partial}{\partial X}\frac{\partial \lambda^{(1)}}{\partial T}(X_w,T_1)\left(\frac{1}{X_w}+D\right)-\frac{\partial \lambda^{(1)}}{\partial T}(X_w,T_1)\left(\frac{1}{X_w}+\frac{D}{X_w}\right)-\frac{\partial \lambda^{(1)}}{\partial T}(X_w,T_1)\frac{1}{X_w^{\,2}}\right\}
\end{aligned}
$$

$$-\frac{\partial C_m^{(2)}}{\partial T}(X_w,T_1)\left\{\frac{\partial\lambda^{(2)}}{\partial X}(X_w,T_1)D-\lambda^{(2)}(X_w,T_1)\frac{D}{X_w}\right\}$$

$$-C_m^{(2)}(X_w,T_1)\left\{\frac{\partial}{\partial X}\frac{\partial\lambda^{(2)}}{\partial T}(X_w,T_1)D-\frac{\partial\lambda^{(2)}}{\partial T}(X_w,T_1)\frac{D}{X_w}\right\} \qquad \text{(F.3)}$$

Similarly the second derivative of $\mathcal{L}$ with respect to T_2 is,

$$\begin{aligned}
\frac{\partial^2}{\partial T_2{}^2}\mathcal{L} &= \frac{\partial f}{\partial T}\left[T_2,0,C_m^{(2)}(X_w,T_2)\right]+\frac{\partial f}{\partial C}\left[T_2,0,C_m^{(2)}(X_w,T_2)\right]\frac{\partial C_m^{(2)}}{\partial T}(X_w,T_2)\\
&-\frac{\partial f}{\partial T}\left[T_2,1,C_m^{(3)}(X_w,T_2)\right]-\frac{\partial f}{\partial C}\left[T_2,1,C_m^{(3)}(X_w,T_2)\right]\frac{\partial C_m^{(3)}}{\partial T}(X_w,T_2)\\
&+\int_{X_w}^{\infty}\frac{\partial C_m^{(2)}}{\partial T}(X,T_2)\left\{\begin{array}{l}\dfrac{\partial\lambda^{(2)}}{\partial T}(X,T_2)+\dfrac{\partial^2}{\partial X^2}\left[\lambda^{(2)}(X,T_2)D\right]-\dfrac{\partial}{\partial X}\left[\lambda^{(2)}(X,T_2)\dfrac{D}{X}\right]\\ -\beta\alpha\lambda^{(2)}(X,T_2)+\alpha^2\beta e^{\alpha T_2}\left[\int_{T_2}^{T_3}e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\right]\end{array}\right\}dX\\
&+\int_{X_w}^{\infty}C_m^{(2)}(X,T_2)\left\{\begin{array}{l}\dfrac{\partial^2\lambda^{(2)}}{\partial T^2}(X,T_2)+\dfrac{\partial^2}{\partial X^2}\dfrac{\partial\lambda^{(2)}}{\partial T}(X,T_2)D-\dfrac{\partial}{\partial X}\left[\dfrac{\partial\lambda^{(2)}}{\partial T}(X,T_2)\dfrac{D}{X}\right]\\ -\beta\alpha\dfrac{\partial\lambda^{(2)}}{\partial T}(X,T_2)+\alpha^3\beta e^{\alpha T_2}\left[\int_{T_2}^{T_3}e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\right]\\ -\alpha^2\beta e^{\alpha T_2}\left[e^{-\alpha T_2}\lambda^{(3)}(X,T_2)\right]\end{array}\right\}dX\\
&-\int_{X_w}^{\infty}\frac{\partial C_m^{(3)}}{\partial T}(X,T_2)\left\{\begin{array}{l}\dfrac{\partial\lambda^{(3)}}{\partial T}(X,T_2)+\dfrac{\partial^2}{\partial X^2}\left[\lambda^{(3)}(X,T_2)\left(\dfrac{1}{X}+D\right)\right]-\dfrac{\partial}{\partial X}\left[\lambda^{(3)}(X,T_2)\left(\dfrac{1}{X}+\dfrac{D}{X}\right)\right]\\ -\beta\alpha\lambda^{(3)}(X,T_2)+\alpha^2\beta e^{\alpha T_2}\left(\int_{T_2}^{T_3}e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\right)\end{array}\right\}dX\\
&-\int_{X_w}^{\infty}C_m^{(3)}(X,T_2)\left\{\begin{array}{l}\dfrac{\partial^2\lambda^{(3)}}{\partial T^2}(X,T_2)+\dfrac{\partial^2}{\partial X^2}\left[\dfrac{\partial\lambda^{(3)}}{\partial T}(X,T_2)\left(\dfrac{1}{X}+D\right)\right]-\dfrac{\partial}{\partial X}\left[\dfrac{\partial\lambda^{(3)}}{\partial T}(X,T_2)\left(\dfrac{1}{X}+\dfrac{D}{X}\right)\right]\\ -\beta\alpha\dfrac{\partial\lambda^{(3)}}{\partial T}(X,T_2)+\alpha^3\beta e^{\alpha T_2}\left(\int_{T_2}^{T_3}e^{-\alpha t}\lambda^{(3)}(X,t)\,dt\right)-\alpha^2\beta e^{\alpha T_2}\left(e^{-\alpha T_2}\lambda^{(3)}(X,T_2)\right)\end{array}\right\}dX\\
&-D\frac{\partial C_m^{(2)}}{\partial T}(\infty,T_2)\left[\lambda^{(2)}(\infty,T_2)+\frac{\partial\lambda^{(2)}}{\partial X}(\infty,T_2)\right]-DC_m^{(2)}(\infty,T_2)\left[\frac{\partial\lambda^{(2)}}{\partial T}(\infty,T_2)+\frac{\partial}{\partial X}\frac{\partial\lambda^{(2)}}{\partial T}(\infty,T_2)\right]\\
&+D\frac{\partial C_m^{(3)}}{\partial T}(\infty,T_2)\left[\lambda^{(3)}(\infty,T_2)+\frac{\partial\lambda^{(3)}}{\partial X}(\infty,T_2)\right]+DC_m^{(3)}(\infty,T_2)\left[\frac{\partial\lambda^{(3)}}{\partial T}(\infty,T_2)+\frac{\partial}{\partial X}\frac{\partial\lambda^{(3)}}{\partial T}(\infty,T_2)\right]\\
&+\frac{\partial C_m^{(2)}}{\partial T}(X_w,T_2)\left\{\frac{\partial\lambda^{(2)}}{\partial X}(X_w,T_2)D-\lambda^{(2)}(X_w,T_2)\frac{D}{X_w}\right\}
\end{aligned}$$

$$
\begin{aligned}
&+C_m^{(2)}(X_w,T_2)\left\{\frac{\partial}{\partial X}\frac{\partial\lambda^{(2)}}{\partial T}(X_w,T_2)D-\frac{\partial\lambda^{(2)}}{\partial T}(X_w,T_2)\frac{D}{X_w}\right\} \\
&-\frac{\partial C_m^{(3)}}{\partial T}(X_w,T_2)\left\{\frac{\partial\lambda^{(3)}}{\partial X}(X_w,T_2)\left(\frac{1}{X_w}+D\right)-\lambda^{(3)}(X_w,T_2)\left(\frac{1}{X_w}+\frac{D}{X_w}\right)-\lambda^{(3)}(X_w,T_2)\frac{1}{X_w{}^2}\right\} \\
&-C_m^{(3)}(X_w,T_2)\left\{\frac{\partial}{\partial X}\frac{\partial\lambda^{(3)}}{\partial T}(X_w,T_2)\left(\frac{1}{X_w}+D\right)-\frac{\partial\lambda^{(3)}}{\partial T}(X_w,T_2)\left(\frac{1}{X_w}+\frac{D}{X_w}\right)-\frac{\partial\lambda^{(3)}}{\partial T}(X_w,T_2)\frac{1}{X_w{}^2}\right\}
\end{aligned}
\tag{F.4}
$$

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Vita

Captain Richard Thomas Hartman was born in Joliet, Illinois on 22 April 1966. He graduated from the University of South Florida with a Bachelor of Science degree in Physics and was commissioned in the United States Air Force through the four year ROTC program, April 1988. As a research physicist at the Armstrong Laboratory, he developed innovative measurement methods, techniques, and measuring equipment for evaluating all types of Night Vision Systems. This work resulted in the only Department of Defense facility with the capability to objectively measure night vision goggles as a whole component. During this assignment he noticed the current and future challenges associated with the prevention, control, and abatement of past, present, and future environmental problems and successfully met a competitive category transfer board to become a Bioenvironmental Engineer. As a Bioenvironmental Engineer at Wright Patterson AFB he positively affected both the occupational and environmental community and was selected as the Bioenvironmental Fellow in Occupational Health, Environmental Protection and Radiation Protection Management at Bolling AFB, Washington DC.

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13. ABSTRACT *(Maximum 200 words)*

The remediation of groundwater contamination continues to persist as a social and economic problem due to increased governmental regulations and public health concerns. Additionally, the geochemistry of the aquifer and the contaminant transport within the aquifer complicates the remediation process to restore contaminated aquifers to conditions compatible with health-based standards. Currently, the preferred method for aquifer cleanup (pump-and-treat) has several limitations including, the persistence of sorbed chemicals on soil matrix and the long term operation and maintenance expense. The impetus of this research was to demonstrate that a calculus of variations approach could be applied to a pulsed pumping aquifer remediation problem where contaminant transport was affected by rate-limited sorption and generalized to answer several management objectives. The calculus of variation approach produced criteria for when the extraction pump is turned on and off. Additionally, the analytic solutions presented in this research may be useful in verifying numerical codes developed to solve optimal pulsed pumping aquifer remediation problems under conditions of rate-limited sorption.

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